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THE

PHYSICAL REVIEW.

THE DETECTING EFFICIENCY OF THE RESISTANCE-CAPACITY COUPLED ELECTRON TUBE AMPLIFIER.

By E. O. Hulburt.

Synopsis.

Detecting efficiency of the resistance-capacity coupled, two tube amplifier.—A theoretical formula is derived and compared with the results of *measurements* made by using a condenser potential divider to vary the high frequency input voltage A and a sensitive galvanometer to measure the rectified high frequency component of the output plate current b_0, the detecting efficiency being defined as b_0/A^2. Satisfactory agreement was found for the *various frequencies and coupling capacities* tried. The *effect of a third tube* was determined experimentally. For convenience of *comparison with transformer-coupled amplifiers*, curves are given showing the detecting efficiencies of the various amplifiers as a function of the frequency and hence their relative merits in detecting unmodulated signals.

Current amplification of the above amplifier as a function of the frequency was also determined.

1. Introductory.

THE detecting efficiency of the electron tube amplifier means, in general words, the efficiency of the amplifier to make weak signals intelligible. From general considerations it can be seen that the detecting efficiency depends upon the relation between the input grid voltage change, and the resulting change in the output plate current. This has already been discussed in two papers,[1] one of which dealt with experimental measurements of the detecting efficiency of a three tube high-frequency transformer-coupled amplifier, and the other with the detecting efficiency of the single electron tube; this last considered the question from both a theoretical and an experimental standpoint. In the case of the high-frequency transformer-coupled amplifier the detecting efficiency was defined by the relation $\lim_{A \doteq 0} b_0/A^2$ where A and b_0 are the amplitudes, respectively, of the input grid potential and of the

[1] Phys. Rev., 16, 274, 1920; 16, 408, 1920.

rectified component of the output plate current. In the present paper is described an investigation, both theoretical and experimental, of the detecting efficiency of the high frequency resistance-capacity coupled amplifier. A theoretical analysis, in which certain simplifying assumptions were made, has been carried out, which showed how the detecting efficiency depended upon the constants of the coupling circuits. Experiments were then performed to obtain data on this type of amplifier, and to test the theoretical relations.

2. THEORETICAL.

Consider the high frequency amplifier of two tubes with resistance-capacity coupling as shown in Fig. 1. This amplifier may be used to receive modulated radio-frequency signals. There are other types of resistance-capacity coupling than the one shown in Fig. 1. For example,

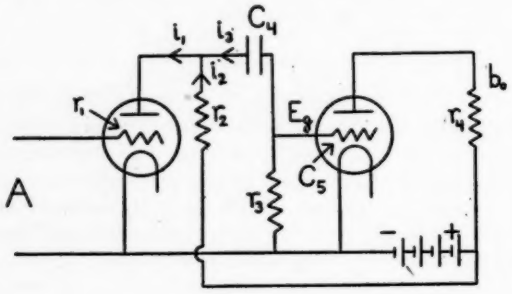

Fig. 1.

if separate plate batteries are used for the two tubes, the capacity C_4 and resistance r_3 may be omitted. Such an amplifier will, in general, possess different characteristics from those of the amplifier of Fig. 1. However, the connections shown in Fig. 1 are commonly used and it is this type of connection which was chosen for this investigation.

Let A be the amplitude of the radio frequency voltage impressed on the grid of the first tube, and let b_0 be the rectified component of the resulting radio frequency current in the plate circuit of the second tube. We now consider the action of the amplifier in the following way. Due to A, a high frequency component of the plate current of the first tube is produced. Call this i_1. This current divides into i_2 and i_3, as shown in Fig. 1. i_3 impresses a high frequency potential oscillation E_g on the grid of the second tube, which in turn causes the rectified high frequency component b_0 of the plate current of the second tube. Amplification is considered to take place in both tubes, but rectification to occur only in the second tube. If rectification occurs in the first tube, this may re-

sult in a shift of the operating point of the grid of the second tube, and hence a change in the characteristics of the amplifier. Experiment has shown, however, that for small input voltages the rectifying effect of the first tube is small, and so in the present treatment it is justifiable to ignore this effect.

We proceed to derive the relation between A and b_0 in terms of the constants of the circuits and of the tubes. Let r_1 be the internal resistance between the filament and the plate of the first tube. Let C_5 be the filament-grid capacity of the second tube. Resistances r_2 and r_3, and capacity C_4 are as shown in Fig. 1. Let $\omega/2\pi$ be the frequency of the impressed voltage.

Let

$$\begin{aligned} \frac{1}{r_1} &= g_1, \qquad \omega C_4 = x_4, \\ \frac{1}{r_2} &= g_2, \qquad \omega C_5 = x_5, \\ \frac{1}{r_3} &= g_3. \end{aligned} \tag{1}$$

Consider the first tube. If the grid-plate capacity of this tube is neglected, it has been shown[1] that the relation between the impressed grid voltage A and the resulting high-frequency component i_1 of the plate current is given by the relation

$$i_1 = \frac{kA}{\frac{1}{g_1} + Z_p}, \tag{2}$$

k is the amplification constant of the tube, and Z_p the impedance of the plate circuit external to the tube. The amplification constant k and the internal resistance $1/g_1$ of tube are real quantities, and not complex, in the case of zero grid-filament capacity.

Considering the circuit shown in Fig. 1, the value of Z_p is found to be

$$Z_p = \frac{1}{g_2 + \frac{1}{\frac{1}{jx_4} + \frac{1}{g_3 + jx_5}}}, \tag{3}$$

where $j = \sqrt{-1}$. Substituting (3) in (2) gives

$$i_1 = kAg_1 \frac{g_2g_3 - x_4x_5 + j[x_4(g_2 + g_3) + x_5g_2]}{g_2g_3 - x_4x_5 + g_1g_3 + j[x_4(g_1 + g_2 + g_3) + x_5(g_1 + g_2)]}.$$

The modulus of this is

$$i_1 = kAg_1 \sqrt{\frac{(g_2g_3 - x_4x_5)^2 + [x_4(g_2 + g_3) + x_5g_2]^2}{(g_2g_3 - x_4x_5 + g_1g_3)^2 + [x_4(g_1 + g_2 + g_3) + x_5(g_1 + g_2)]^2}}, \tag{4}$$

[1] G. Breit, PHYS. REV., 16, 388, 1920. Others have given similar formulas.

where i_1 now stands for the root-mean square value of the high frequency plate current of the first tube. It should be noticed that in the above treatment conductance through the coupling condenser C_4 has been neglected. The measured direct current value of this resistance was over 50 megohms. Terms expressing this condenser leakage were introduced into formula (4), but were found to be negligible.

Let us turn our attention to what takes place in the coupling circuit and find the relation between i_1 and E_g, the high frequency voltage impressed on the grid of the second tube. From Kirchhoff's laws

$$i_1 = i_2 + i_3,$$
$$\frac{i_2}{g_2} = i_3\left(\frac{1}{jx_4} + \frac{1}{g_3 + jx_5}\right),$$
$$E_g = \frac{i_3}{g_3 + jx_5}.$$

It is assumed that the grid-filament conduction current of the second tube is zero. Then

$$E_g = \frac{i_1}{(g_3 + jx_5)\left\{1 + g_2\left(\frac{1}{jx_4} + \frac{1}{g_3 + jx_5}\right)\right\}}.$$

The modulus of this is

$$E_g = \frac{i_1}{\left\{\left(g_2 + g_3 + \frac{x_5}{x_4}g_2\right)^2 + \left(x_5 - \frac{g_2g_3}{x_4}\right)^2\right\}^{1/2}}. \tag{5}$$

In this expression E_g stands for the root-mean-square value of the grid voltage of the second tube.

Consider now the second tube, in which amplification and rectification both occur. It has been shown experimentally in the previous papers[1] that the relation

$$\frac{b_0}{E_g^2} = n \tag{6}$$

is approximately true, where n is a quantity which is independent of the magnitude of E_g. It is assumed that in the present case n did not depend upon the frequency of the impressed voltage, because the impedance of the plate circuit of the second tube was independent of the frequency. This assumption was subsequently justified by experiment.

Introducing (4) and (5) into (6) we have

$$\frac{b_0}{A^2} = nk^2g_1^2\,\frac{(g_2g_3 - x_4x_5)^2 + [x_4(g_2 + g_3) + x_5g_2]^2}{(g_2g_3 - x_4x_5 + g_1g_3)^2 + [x_4(g_1 + g_2 + g_3) + x_5(g_1 + g_2)]^2}\cdot\frac{}{\left(g_2 + g_3 + \frac{x_5}{x_4}g_2\right)^2 + \left(x_5 - \frac{g_2g_3}{x_4}\right)^2}. \tag{7}$$

[1] *Loc. cit.*

This expression gives the desired relation between the detecting efficiency b_0/A^2 and the constants of the tubes and of the circuits. In the former papers[1] the detecting efficiency has been defined by the relation $\lim_{A=0} b_0/A^2$. Although this is theoretically the proper definition (because it avoids any possibility of rectification in the first tube), we have been content in the present instance to measure the value of b_0/A^2 for finite values of A, and to call this the detecting efficiency.

3. Apparatus.

The apparatus consisted of a condenser potential divider, the amplifier, and a D'Arsonval galvanometer connected in the plate circuit of the last tube. These will be described in the order named. The arrangement is shown schematically in Fig. 2. The condenser potential divider

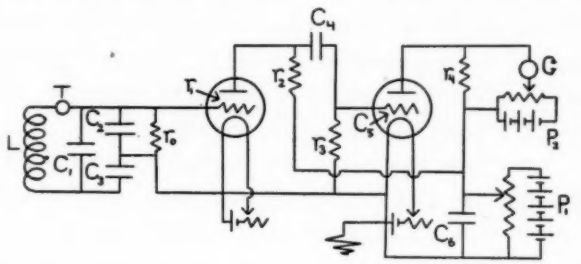

Fig. 2.

consisting of the three condensers c_1, c_2, c_3, the inductance coil L, and the thermogalvanometer T, were the same as described in a previous paper.[2] By coupling L to a suitable electron tube generating set, unmodulated high frequency voltage of small known amplitude and frequency was impressed on the grid of the first electron tube. The high resistance leak r_0 (1.2×10^6 ohms) was connected across c_2 to ensure a definite value of the grid potential during the experiment. The effect of r_0 upon the impedance of c_2 was negligible because c_2 was large (about 0.05 $\mu F\delta$) and the frequencies used were of the order of 3×10^5.

The amplifier was a two-tube one with resistance-capacity coupling. The tubes were Western Electric Company tubes, Type VTI; they were used with the filament current always 1.10 amperes and the plate voltage always 23.7 volts. Separate storage cells supplied each filament; the plate voltage supply was common to all the tubes. The plate battery was shunted by a 2 μF condenser c_6. The resistance r_2 was 27.6×10^3 ohms and r_3 was 393×10^3 ohms. The resistances r_0, r_2 and r_3, were

[1] *Loc. cit.*

[2] *Loc. cit.*

non-inductive. A resistance unit was made by painting both sides of a strip of cardboard about 4 mm. wide with black drawing ink. Two sturdy brass clips were pinched on to each end of the strip, so that the length of the strip between the jaws was about 0.5 mm. This was sealed in a small glass tube with sealing wax, the connecting wires being soldered to the brass clips and brought out through the wax seals. Such a resistance when well made, was found to change in value by not more than ten per cent. in two months. The resistance of 30,000 ohm units was found to be appreciably constant for direct currents varying from 10^{-4} to 10^{-5} amperes. The currents which they carried in the amplifier never exceeded these values. The high frequency resistance of a unit was assumed to be the same as the resistance found by a direct current measurement.

The change in the value of the rectified high frequency component of the plate current of the second tube of the amplifier (which we have designated by b_0) was measured by a D'Arsonval galvanometer, G, Fig. 2, connected across a resistance r_4, placed in the plate circuit. r_4 was 60,000 ohms. The galvanometer had a resistance of 16 ohms and a sensibility of 1.7×10^{-9} amperes per millimeter deflection at a scale distance of 120 cm. P_1 and P_2, Fig. 2, were potential dividers, P_1 serving to keep the plate voltage at a standard value, and P_2 to compensate for the potential drop in the resistance r_4, so that the galvanometer rested approximately at zero. When the input grid voltage was changed, a deflection of the galvanometer resulted which was proportional to the change in the rectified high frequency component of the output plate current.

It was important that the filament voltage of the last tube and the voltages of P_1 and P_2 be constant. When a slow drift of the galvanometer occurred, the error was eliminated by averaging deflections. To insure that high frequency currents were not causing unknown disturbances in the galvanometer the following test was made. The deflection was observed with a certain voltage impressed on the amplifier. A 2 μF condenser was then connected across the galvanometer terminals, and it was found that the deflection remained unchanged. This showed that the high frequency currents did not appreciably affect the galvanometer.

4. The Two-Tube Amplifier.

(*a*) *The Variation of the Detecting efficiency with the Coupling Capacity.*—With the arrangement of apparatus as shown in Fig. 2, the resistances r_2 and r_3 were varied until the value of b_0 for a specified A at a frequency

of 3×10^5 was approximately a maximum. This adjustment was not critical, and the values of r_2 and r_3 finally chosen were 27.6×10^3 and 393×10^3 ohms, respectively. After this was done the values of b^0 were observed for a series of values of A and for a series of values of the coupling condenser C_4. The values of b_0, shown in the family of

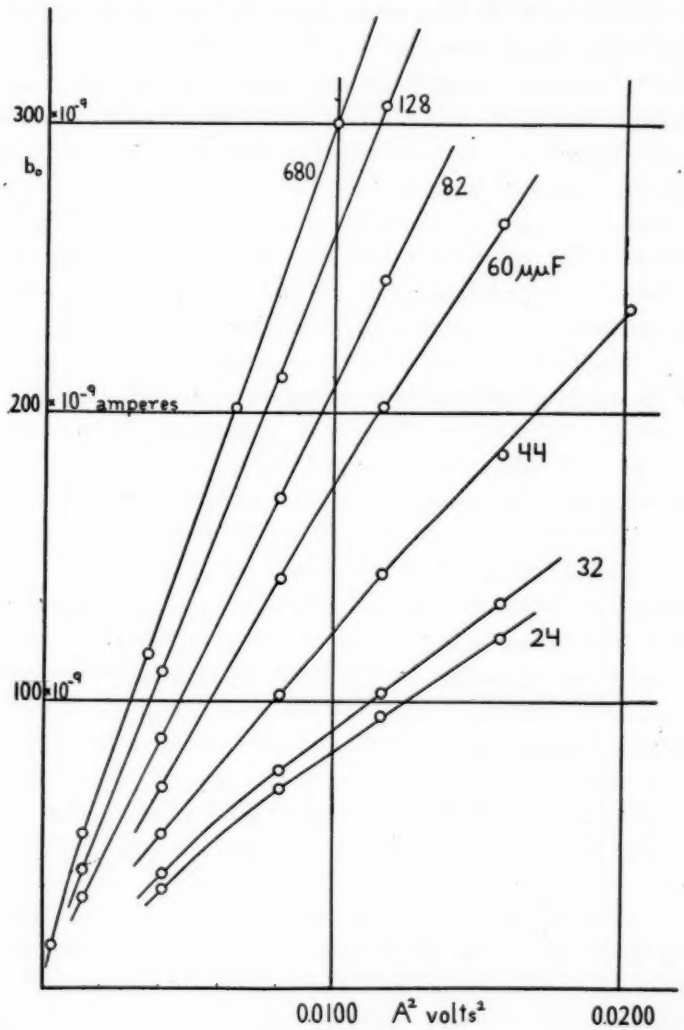

Fig. 3.

curves in Fig. 3, have been plotted as ordinates against the values of A^2 as abscissas. The frequency used was 3×10^5, corresponding to a wave-length of 1,000 m. It is seen that b_0 is approximately proportional to A^2, which is a first check on the correctness of formula (7). The fact that b_0 was approximately proportional to A^2 meant that the action

of the last electron tube was represented approximately by the expansion of the plate-current grid-voltage relation, by Taylor's theorem, in which derivatives of higher order than the second were neglected. The slight bends in the lines of Fig. 3 may perhaps be ascribed to rectification occurring in the first tube, as discussed in section 2.

To see further to what extent the assumptions underlying (7) were in agreement with experiment, the values of b_0/A^2 for each value of C_4 in Fig. 3, for $A^2 = 0.010$ volts^2, have been plotted as ordinates against C_4 as abscissas in the full line curve of Fig. 4. In all cases the ratio b_0/A^2 has been expressed in amperes divided by volts^2. The numerical values of the circuit constants were as follows: $r_1 = 65 \times 10^3$ ohms, $r_2 = 27.6 \times 10^3$ ohms, $r_3 = 393 \times 10^3$ ohms, $\omega = 6\pi \times 10^5$, $C_4 = 680\ \mu\mu$F, and $C_5 = 38\ \mu\mu$F. The value for r_1 had been previously determined for this electron tube by measurements of its direct current characteristics for the filament and plate voltages used in these experiments. The value of C_5, *i.e.*, 38 $\mu\mu$F, was found by a measurement of the grid-to-filament capacity *in situ*, and included the capacity of the tube socket and connecting wires. Introducing the above values of the quantities into equation (7), and using the observed value of b_0/A^2, *i.e.*, 30×10^{-6}, for $C_4 = 680\ \mu\mu$F, the values of b_0/A^2 were computed for a series of values of C_4 from 680 to 10 $\mu\mu$F. The theoretical curve is shown in the dotted line of Fig. 4. The two curves agree closely for values of C_4 from 680 $\mu\mu$F to 200 $\mu\mu$F. For C_4 below 200 $\mu\mu$F the observed values of the detecting efficiency are seen to be less than the theoretical values.

If the more exact formula for the detecting efficiency had been used, *i.e.*, $\lim_{A \doteq 0} b_0/A^2$, instead of the formula b_0/A^2 where $A^2 = 0.010$ volts^2, the agreement between the observed and the theoretical detecting efficiencies would perhaps have been better. The data of Fig. 3 indicate this. At all events the agreement is sufficiently good to show that the simple theory embodied in formula (7) is an approximate statement of the facts.

(*b*) *The Variation of the Detecting Efficiency with the Frequency.*—The detecting efficiency of the amplifier was measured for a number of frequencies of the input voltage A. The coupling condenser C_4 was kept at its largest value, 680 $\mu\mu$F, throughout this series of measurements. The other capacities and resistances of the amplifier were the same as before. The values of A^2 were between 0.005 and 0.012 volts^2. The values of b_0/A^2, computed from the observed values of b_0 and A^2, have been plotted against wave-length in Fig. 5 for a range of wave-lengths from 400 to 1,600 meters. The points are shown as small circles in the figure; a smooth line, curve 1, has been drawn through them. The

theoretical curve, computed from formula (7), is shown in the dotted curve 2, Fig. 5. This curve has been made to agree with the observed one at the wave-length 1,000 meters. The agreement between the theoretical and observed curves is good, and shows that formula (7) represents the behavior of the amplifier with fair accuracy.

(*c*) *Amplification.*—To determine the amplification due to the use of the first tube the detecting efficiency of the second tube alone was measured. This was done by disconnecting the first tube entirely and impressing the input voltage directly on the grid of the second tube. The values thus found for each wave-length are plotted in Curve 3,

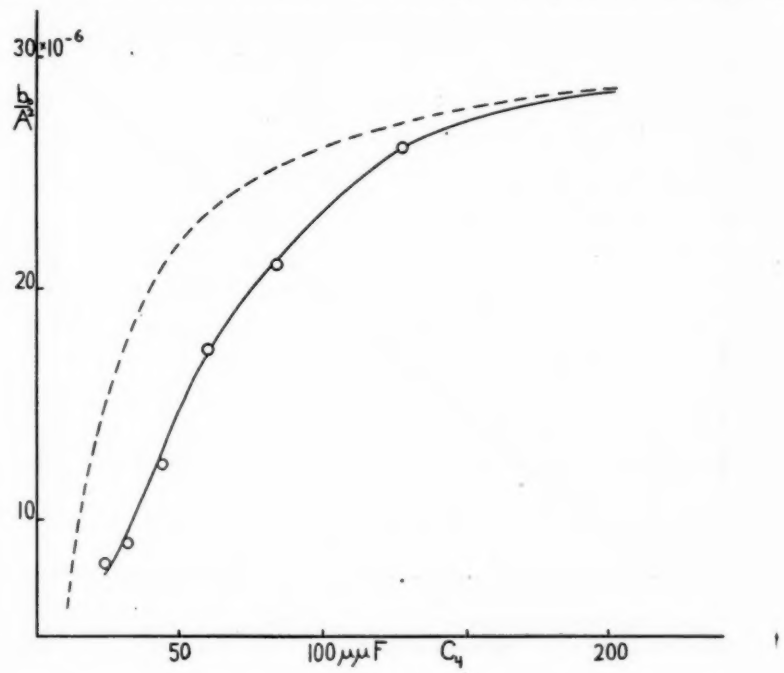

Fig. 4.

Fig. 5. It is seen that the detecting efficiency of the second tube in this case was appreciably constant with wave-length. This bears out the assumption underlying formula (6). By dividing the ordinates of curve 1 by those of curve 2, Fig. 5, for the same wave-length, the amplification of the rectified high frequency component b_0 of the plate current of the second tube due to the use of the first tube with the resistance-capacity coupling was determined. Since the detecting efficiency of the second tube, when alone, was 10×10^{-6}, the curve 1, Fig. 5, also shows the amplification. The marginal numbers on the right of Fig. 5 refer to the amplification. These numbers give the *current* amplification. The

power amplification or, if telephones are used, the *sound intensity* amplification is proportional to the square of these numbers.

5. COMPARISON WITH OTHER AMPLIFIERS.

A third tube was coupled to the two-step amplifier by means of resistance-capacity coupling. The plate resistance of this coupling was 19.4×10^3 ohms, the grid resistance was 134×10^3 ohms, and the coupling capacity was 680 $\mu\mu$ F. These correspond to r_2, r_3 and C_4 of Fig. 2, respectively. The detecting efficiency of this three-tube ampli-

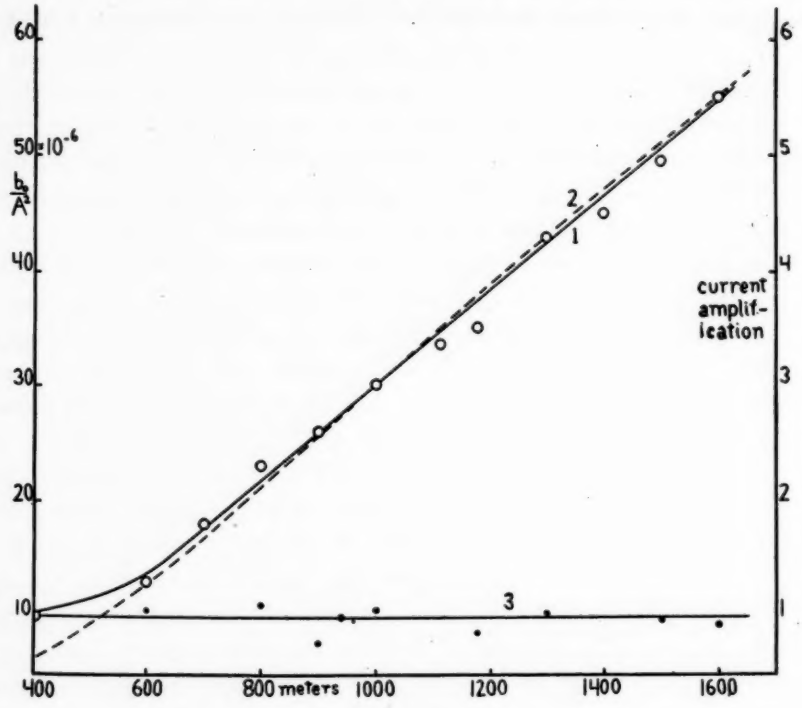

Fig. 5.

fier was measured for the wave-length range from 400 to 1600 meters. The curve is shown in curve 2, Fig. 6. Curves 1 and 3, Fig. 6, are reproductions of curves 1 and 3, Fig. 5, and refer to the two and one tube amplifiers respectively; they are placed in Fig. 6 for the sake of comparison. It is seen that for wave-lengths below 500 meters the addition of one and two tubes with resistance capacity coupling to the single detector tube produced no increase in amplification.

To show the comparison with a transformer-coupled amplifier data from a former paper[1] have been used and have been plotted in curves

[1] PHYS. REV., 16, 274, 1920. It should be noted that in Fig. 3 of this paper the number 15 should be 1.5.

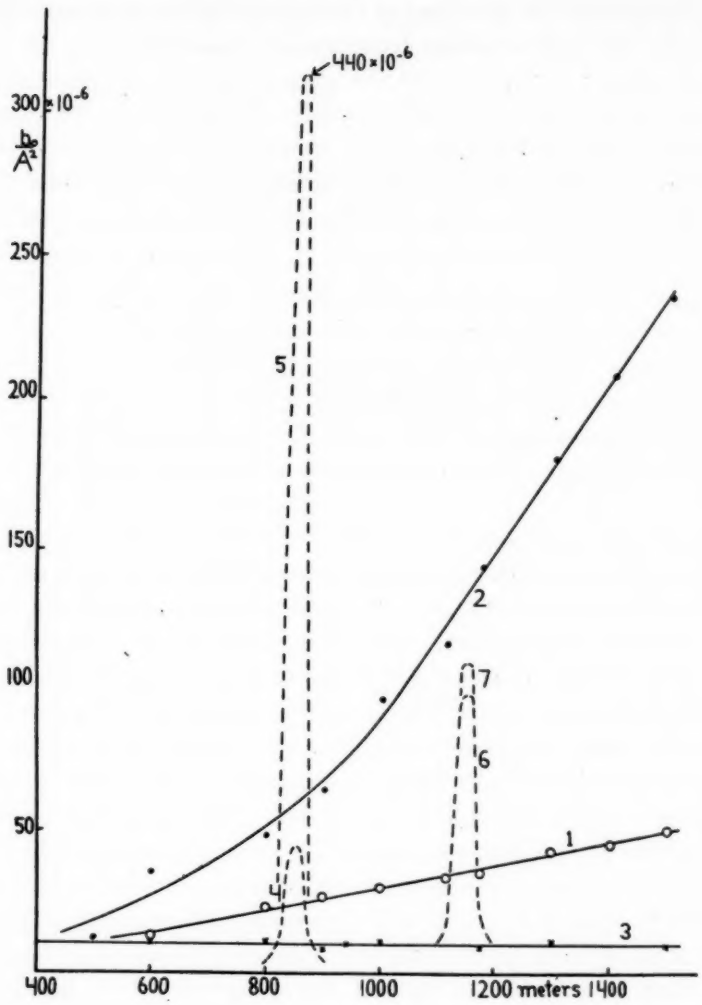

Fig. 6.

4 and 5, Fig. 6. These curves refer to a two-tube and a three-tube amplifier, respectively. The two-tube amplifier consisted of two tubes connected by a high frequency air (wood) core transformer tuned to a wave-length of 850 meters. The transformer was made of No. 36 silk-covered copper wire wound on paraffined wooden spools 3 cm. in diameter, 200 turns on the primary and 250 turns on the secondary. The detector tube of this amplifier was a different one from that of the two-tube resistance-capacity amplifier of curve 1, b_0/A^2 being 4.4×10^{-6}, whereas in the resistance capacity case b_0/A^2 was 10×10^{-6}; so that the curves 1 and 4 are merely an over-all comparison of the two ampli-

fiers. The three-tube amplifier of curve 5 was made by coupling a third tube to the two-tube amplifier by a similar transformer.

A more direct comparison of the performance of resistance-capacity coupling and transformer coupling was carried out in the following way. By means of two double-pole double-throw switches it was arranged so that either the resistance-capacity coupling or the transformer coupling could be used in turn. Fig. 7 shows the connections. When the re-

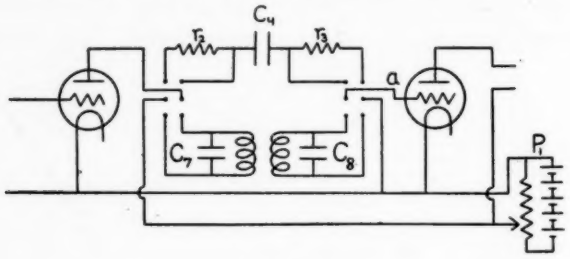

Fig. 7.

sistance-capacity coupling was used the amplifier was the same as that used above for curve 1, Fig. 6. The transformer coupling consisted of a tuned air core transformer. This was made of No. 36 silk-covered copper wire wound on paraffined wooden spools 3 cm. in diameter, 225 turns on the primary and 275 turns on the secondary. The primary was tuned by a small air condenser, c_7, Fig. 7, of capacity 37 $\mu\mu$F, and the secondary by another condenser c_8, of capacity 32 $\mu\mu$F. The transformer was tuned to a wave-length 1,150 meters. The detecting efficiency of this amplifier for various wave-lengths is shown by curve 6, Fig. 6. In order to make this comparison the procedure was as follows: With no impressed voltage A on the grid of the first tube the potential divider P_2, Fig. 2, was adjusted so that the galvanometer rested approximately at zero. Then A was turned on and the deflection of the galvanometer noted. The transformer coupling was then thrown in by means of the double-throw switches. It was found necessary to readjust P_2 by as much as perhaps 0.05 volts, and when A was turned on, the deflection was in the *opposite* direction to what it had been before in the case of the resistance capacity coupling. This meant that the grid potential of the second tube was not the same for the two cases, and hence that the detector tube was operating upon two different points on the grid-plate characteristic curve, one point being on a concave portion of the curve and the other on a convex portion. As a result curves 6 and 1, Fig. 6, do not necessarily show the true comparison between the two methods of coupling. To obtain a better comparison a voltage was inserted at point a, Fig. 7, with the negative terminal connected to the

grid. Using the resistance-capacity coupling the voltage at a was adjusted until the galvanometer deflection, due to A, had the same absolute value as before, but in the opposite direction. The voltage at a was 1.10 volts. The deflection was now in the same direction as for the transformer coupling. Further, it was found that only a small readjustment of P_2 was required in changing from one coupling to the other. This meant that the detector was being used at approximately the same operating point in the two cases. The values of the detecting efficiency of the transformer-coupled amplifier were now found to be about ten per cent. greater than the values given in curve 6, Fig. 6, and are shown in curve 7, Fig. 6. Curves 7 and 1 exhibit the comparison between the two methods of coupling under approximately similar conditions. It should be noticed that Fig. 6 portrays in a clear manner the relative merits of a number of amplifiers as far as their detecting efficiency for an unmodulated voltage is concerned.

In conclusion the author finds pleasure in expressing his thanks to Mr. W. G. Brombacher for valuable assistance in carrying out the experimental arrangements.

Johns Hopkins University,
January, 1921.

AN ACOUSTICAL GALVANOMETER FOR THE MEASUREMENT OF SMALL ALTERNATING CURRENTS.

BY F. R. WATSON AND L. B. HAM.

SYNOPSIS.

Acoustic Alternating Current Galvanometer.—(1) *Description.* By sending the current through a telephone receiver, magnifying the emitted sound by means of a double resonator and measuring the intensity of the sound by means of a Rayleigh disk hung in the tube connecting the resonating chambers, a measure of the alternating current is obtained in terms of the rotation of the disk. (2) *Variation of the sensitivity with frequency* was investigated with the help of a hot wire ammeter. For the particular instrument studied maxima were found at frequencies of the resonator and telephone diaphragm. The sensitivity for 510 was about 5.7×10^{-8} amperes. Probably a much more sensitive instrument could be made by using sharper resonance and a more delicate quartz suspension.

Measurement of intensity of pure telephone sounds could be effected by means of the above instrument if the frequency used is known as well as the corresponding sensitivity.

DESIGN OF INSTRUMENT.

THE design of an acoustical galvanometer was suggested by an earlier investigation where a Rayleigh disc double resonator[1] was used to measure the faint sounds transmitted by plaster partitions.[2]

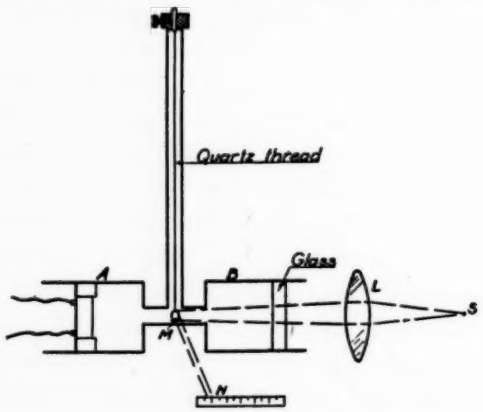

Fig. 1.

Acoustical Galvanometer.

It seemed likely that a response could be obtained if a telephone receiver screwed on the open end of the resonator were used as the source of sound. Fig. 1 pictures the mechanical details of the instrument. *A* and

[1] Lord Rayleigh, "Theory of Sound," Vol. 2, Sec. 253b.

[2] Watson, PHYS. REV., Vol. 15, p. 231, 1920.

B are two chambers of a double resonator connected by a tube. A telephone receiver is screwed tightly to the outer end of chamber A and, by the movement of its plate when an electric current passes, sets up sound vibrations that are amplified by the resonator.[1] Proper proportioning of the parts gives maxima of response and furnishes a means of measuring the alternating currents that actuate the telephone.

Action of the Galvanometer.

The presence of the sound waves is made visible by means of a Rayleigh disc M. This is a thin, plane, circular glass plate which is suspended by a quartz thread in the axis of the connecting tube. Theory shows that a loop of the stationary waves may exist in the connecting tube so that if the disc is placed at an angle to the axis of the tube it will tend to turn flatwise to the alternating currents of air.[2]

Any rotation of the disc is made visible in a quantitative way by the deflection of a beam of light incident on the disc. The beam starts from the lamp S, passes through the lens L, the plate glass B and finally, after reflection from the disc M, to the scale N. These deflections furnish a measure of the alternating currents that actuate the telephone.

Theory.

The frequency of the resonator may be calculated approximately from the theory.[3] The formula for the frequency, N, becomes

$$N = \frac{a}{2\pi}\sqrt{c\left(\frac{1}{S}+\frac{1}{S'}\right)},$$

where a is the velocity of sound, S, the volume of chamber B, S' the volume of the loud speaking telephone, and C, the conductivity, which is equal in this case to the area of cross section of the connecting tube divided by its length. The presence of the Rayleigh disc interferes with the free flow of air and virtually reduces the cross-section of the neck.

[1] The dimensions of the resonator are given as follows: The chamber B was a brass cylinder 5.9 cm. internal diameter and 2.9 cm. long, closed by a plate glass to allow passage of light. The connecting tube was 1.2 cm. internal diameter with a total length of 12.3 cm. while the chamber A consisted of the volume of a Western Electric No. 117W loud-speaking telephone. A quartz thread about 46 cm. long served to suspend the Rayleigh disc, the latter being a thin, plane, microscope cover glass about ¼ inch in diameter. The period of the suspended system was about 2.5 minutes. The pitch of natural resonance was 510. The instrument would give response for sounds of threshold audibility. It seems likely that a better tuning could be obtained if the chambers A and B were made adjustable, that is, have the telephone in A and the glass plate in B each adjustable as a piston. Good results have been obtained in another instrument with chambers A and B of equal volume.

[2] Rayleigh, *loc. cit.*

[3] Rayleigh, Phil. Mag., Vol. 36, p. 231, 1918.

The intensity of the sound I that rotates the disc is related to the deflection of the disc according to the relation:[1] $I = k\varphi \sin 2(\theta - \varphi)$, where k is a constant and θ is constant, equal for most sensitive arrangement to 45°, and φ is the angle of rotation of the disc.

EXPERIMENTAL INVESTIGATION.

The current necessary to operate the acoustical galvanometer was so small that ordinary alternating current ammeters gave no response. The following arrangement was then devised to test the instrument and calibrate it. An alternating current was passed in series through the

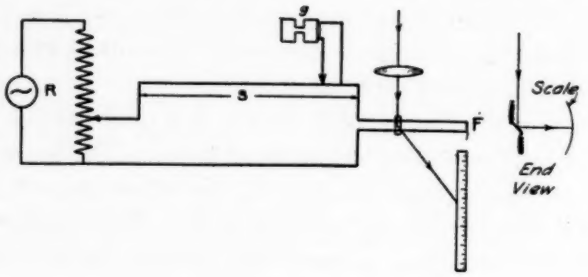

Fig. 2.

Arrangement of apparatus for testing and calibrating the acoustical galvanometer.

resistance S one meter in length and a hot wire ammeter F. Current from S was shunted to actuate the acoustic galvanometer g. The construction of the ammeter F was suggested by Fleming's design[2] and consisted of two manganin wires each one meter long and .003 inches in diameter, mounted parallel to each other 2.5 mm. apart and connected in series, the total resistance being 201.4 ohms. Delicate springs at the center pulled vertically on the wires so that any expansion due to heating when the current passed resulted in an upward motion for one wire and downward for the other. Since the two wires were not in a vertical

TABLE I.

Data for Calibration of Hot Wire Ammeter.

E.M.F. Applied.	Scale Reading.
2.1 volts	1.65 cm.
4.2	5.7
6.3	11.0
8.35	19.6

[1] Watson, PHYS. REV., Vol. 7, p. 125, 1916.

[2] Phil. Mag., Vol. 7, p. 595, 1904.

plane, a tiny mirror mounted across the wires rotated slightly when the wires moved and gave a deflection of a reflected beam of light. The calibration of this ammeter gave the following results when a direct current was used. (See Table I.) The range of the instrument was found to be about 5 to 50 milliamperes.

By using alternating current instead of direct, the acoustical galvanometer could then be calibrated by comparison with the Fleming instrument.

Alternating current was obtained from two sources. In one case the current was generated by means of a tone variator in which a telephone receiver was mounted in the adjustable piston. When air was blown across the mouth of the instrument, sound vibrations were set up and produced varying pressures on the telephone plate, thus generating induced alternating currents. The tone variator was placed in a sound-proof box and blown by air from a constant pressure tank. It had a

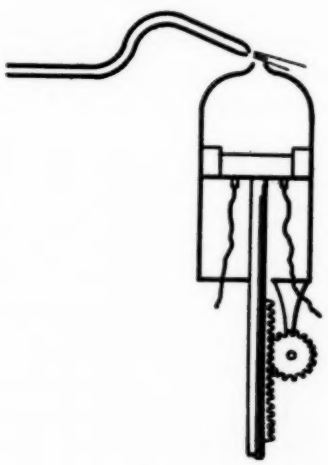

Fig. 3.

Source of Alternating Current.

range of about an octave. When confined to a single pitch it proved satisfactory but when the pitch was varied, the alternating currents were not uniform in intensity, particularly at the extremes of the range. The other source of alternating current was a Siemens and Halske high frequency machine which gave a wider range of pitches with better control of current.

Table II, gives tabulated results obtained with a constant current of varying frequency and Fig. 5 pictures these in a curve.

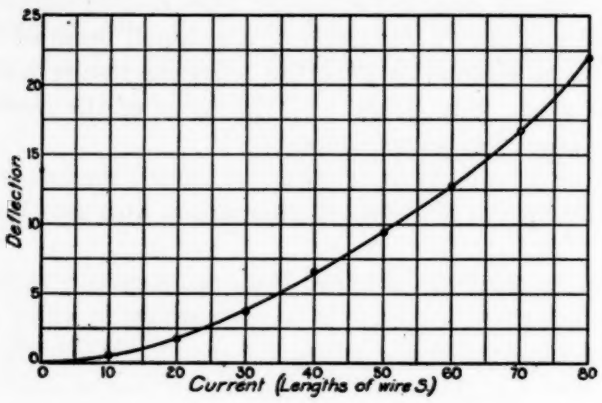

Fig. 4.

Plot Showing Variation of Galvanometer Deflections for Varying Current of Constant Frequency.

TABLE II.

Variation of Deflection with Pitch.

Pitch.....	150	175	200	225	235	250	256	288	350	400	426	450	480
Deflection ..	1.5	3.8	2.7	3.5	6.3	9.5	15.4	5.9	5.0	6.5	14.2	19.2	32.2
Pitch.....	500	512	520	530	540	550	605	645	700	750	775	800	810
Deflection ..	(Off scale)			31.2	24.2	20.2	8.3	6.5	5.7	6.0	8.5	12.7	14.5
Pitch.....	820	830	840	850	878	935	990	1080	1160				
Deflection.....	17.5	20.7	21.3	17.8	6.8	0.9	0.4	0.2	0.0				

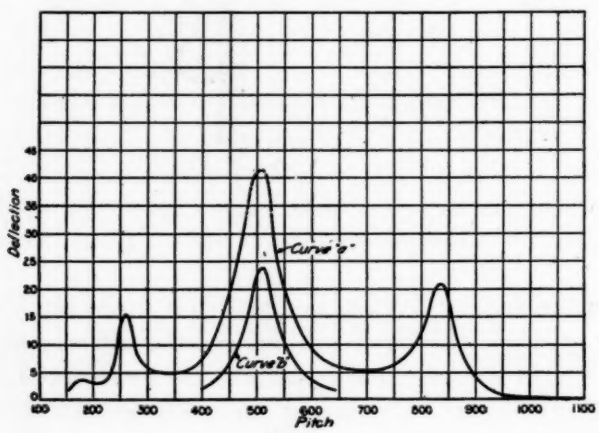

Fig. 5.

Plot Showing Variation of Galvanometer Deflections for Varying Frequency.

Curve *a* shows extreme deflections in the region of 510 frequency, so that a second set of readings was taken with a smaller current to de-

termine the maximum. This data is recorded in Table III. and pictured in curve *b*, Fig. 5.

TABLE III.

Data Showing Resonance for Pitch 510.

Pitch	400	450	470	480	490	500	505	510	515	520
Deflection	2.0	6.7	10.0	15.6	18.2	22.0	23.0	24.0	23.3	22.4
Pitch	530	540	550	560	570	580	590	600	645	
Deflection	17.0	13.7	10.7	8.3	6.9	5.1	4.5	4.3	1.7	

Curve *a* shows three maxima. The maximum for the frequency 510 is due to the natural period of the double resonator as calculated approximately from the theory. The smaller maximum at 256 vibrations, having practically one half the frequency 510, is probably due to a stimulation of the natural vibration of the resonator. The maximum at 840 would appear due to the natural frequency of the telephone plate since such plates have fundamental frequencies in this region.

CALIBRATION OF THE GALVANOMETER.

The calibration of the galvanometer was made for the frequency of 510 vibrations per second. One arrangement of apparatus for this purpose is shown in Fig. 2.

The portion of the resistance S spanned by the galvanometer shunt was .548 ohm and the shunt circuit resistance g 400 ohms, both measured with direct current. When an alternating current of 0.0195 amperes, measured by the hot wire ammeter, flowed in the main circuit, the acoustic galvanometer gave a deflection of 24 divisions, each division being 17.5 mm. wide. The current through the galvanometer was then calculated by the formula:

$$Ig = I \frac{s}{s+g} \text{ to be .00002656 amperes.}$$

For 1 mm. deflection with the scale 1 meter distant from the galvanometer, the current would be:

$$.00002656 \div (24 \times 17.5) = 5.7 \times 10^{-8} \text{ amperes.}$$

This calculation probably does not give the extreme sensitivity of the instrument since the effective resistance of the telephone receiver for alternating current would be greater than 400 ohms as determined by direct current. The calculated result, however, gives an idea of the order of magnitude of the actuating current. Smaller currents could be measured by adjustments of the relative sizes and shapes of the resonator chambers and the connecting neck. Further possibilities for

greater sensitivity are suggested in the coordination of the frequencies of the telephone plate and the resonator, the tuning of the electric circuit with a condenser and in the use of a more delicate quartz thread.

SUGGESTED USES FOR THE INSTRUMENT.

In addition to the measurement of small alternating currents, the instrument may be employed for testing larger currents by using a more robust construction. A portable form of the instrument has been constructed in which the Rayleigh Disc is mounted on a light, stiff pin and the restoring force is furnished by a coiled hair spring attached to the pin. The galvanometer appears promising for use in telephone research where, in a limited sense, it would act as a substitute for the ear and thus measure the actual performance of telephone receivers with varying conditions of current, capacity, and other factors. It would also be useful in psychology tests where quantitative measurements are desired for comparison with the responses of the ear.

LABORATORY OF PHYSICS,
UNIVERSITY OF ILLINOIS,
January, 1921.

EVIDENCE FOR THE EXISTENCE OF HOMOGENEOUS GROUPS OF LARGE IONS.

BY P. J. NOLAN.

SYNOPSIS.

Homogeneous groups of large ions in air.—The existence of such groups, which seemed proved by previous work reported by the author and others, has recently been questioned by the negative results obtained by Blackwood. Hence further experiments have been made using the Zeleny method adopted by Blackwood instead of the McClelland method previously employed. The thirty curves obtained nearly all show two or more peaks or breaks corresponding to definite groups. These peaks came at the same places whether the ions were produced by bubbling the air through alcohol or by passing it over phosphorus. *The mobilities of the groups* agree with the values previously reported within 10 per cent. or less: .050, .025, .018, .0075, .0042, .0025, .0013, .00067, .00033. Some evidence of intermediate groups was also obtained. *In explanation of Blackwood's negative results* it is suggested that since ions are constantly changing from group to group, definite peaks can be expected only if the time spent by each ion in the measuring chamber is relatively short. In Blackwood's experiments this time was from 9 to 150 seconds whereas it was only from 0.5 to 13 seconds in the experiment reported here.

IN various papers[1] published between the years 1916 and 1919 the present writer and others have described experiments showing that, when large ions are produced in air in various ways, the ions can be divided into a number of groups, each group having a definite mobility. In a paper[2] recently published Blackwood presents evidence against the existence of such groups. He finds that the ions distribute themselves continuously over a wide range; in other words he finds "a continuous spectrum of mobilities and not a band spectrum." The present paper gives the results of a reëxamination of the question in the light of Blackwood's criticisms. The evidence here presented is, it is felt, quite convincing as to the existence of the group system and is on the whole a very complete confirmation of previous work.

A short account of the work on group ionization will show that the conclusion that this type of ionization exists was not rashly made. The first indication of groups was obtained in 1912 by J. J. Nolan while working at the electrification caused by spraying water and mention is made of the groups in a paper[3] published in 1914. Before the examina-

[1] J. J. Nolan, Proc. Roy. Irish Acad., Vol. 33, (A), 1916. J. A. McClelland and P. J. Nolan, Proc. Roy. Irish Acad., Vol. 33 (A), p. 24, 1916; Vol. 34 (A), p. 51, 1918; Vol. 35 (A), p. 1, 1919.

[2] Blackwood, PHYS. REV., Aug., 1920.

[3] J. J. Nolan, Proc. Roy. Soc. (A), Vol. 90, 1914.

tion of these groups was completed J. A. McClelland and P. J. Nolan discovered groups in the ionization produced by bubbling air through mercury. When the mobilities were calculated and compared it was found that there was a considerable amount of numerical agreement between the values for the mobilities of various groups. The method of measuring mobilities used was the well-known McClelland method in which the ionized air is drawn along a tube containing an insulated central electrode and curves are plotted between the voltage on the outer tube and the currents to the central electrode. These curves were found to consist of a number of straight lines indicating the presence of distinct groups of ions. The mobilities of the groups were deduced by taking the voltages corresponding to the corners as the saturation voltages for the different groups. The obvious objections to the McClelland method as a method for separating out possible groups of ions of mobilities not widely different were fully realized, but careful consideration failed to account for the experimental results on any other hypothesis than that of the existence of separate groups. Experiments conducted with different methods of producing the air-blast through the mobility tube and also with mobility tubes of different dimensions confirmed the existence of groups. The results on the spray ions and on the ions due to mercury were published at the same time with a joint discussion.

Table I., column A, gives the mobilities of the ions obtained with water and columns B to E give the mobilities observed with mercury with dried and undried air and with long and short time-intervals between production and measurement. It was thought that the mobilities given in columns C, D and E represented groups which were gradually growing and that the final stable sizes were the ions given in columns A and B. The coincidence between the numbers in columns B and D, C and E which are set forth in the table were at the time thought to be accidental. The spray ions did not show any change with time. It was supposed that the ions from mercury took time to add on water vapor, the approach to stable conditions being delayed, in the case of the experiments with partially dried air, by the diminution of the amount of water vapor present.

Further work on the ionization produced by bubbling air through alcohol and by passing air over phosphorus revealed the presence of groups of ions in both cases. In the determination of the mobilities of the various groups the following method was adopted. A preliminary investigation of the current-voltage curve was made and a portion which contained only one corner was selected. This portion was explored very carefully to ensure that it was made up of two intersecting straight lines

TABLE I.

Water.	Mercury.				Alcohol.	Phosphorus.
	Long Time-Interval.		Short Time-Interval.			
	Undried.	Dried.	Undried.	Dried.		
A	B	C	D	E	F	G
1.09					1.10 ?	
.53					.50	
				.32	.31	
.24			.20		.22	.22
.12					.12	
				.092		.092
.046			.048	.043	.049	.053
		.024				.028
.013	.014		.02		.017	.018
		.0068		.0064	.0077	.0074
.0043	.0040		.0045		.0040	.0041
		.0021		.0022	.0023	.0024
.0010	.0013		.0013		.0014	.0012
		.00056			.00063	.00064
.00038	.00034				.00034	.00031
					.00015	.00015
						.000085
						.000053

and to determine the exact point of intersection. In all about 250 such curves were plotted during the course of the alcohol and phosphorus experiments. Table I., column F, gives the mobilities of the ions found in air which had bubbled through alcohol. The results with alcohol caused a modification of the views previously advanced. With alcohol both the series of groups due to water and due to mercury under dry conditions were obtained and no gradual change with time in the mobility of any group was observed in spite of the fact that a large number of observations was taken at a wide range of time-intervals and in the critical manner just described. The agreement of the mobility values as illustrated in Table I. was striking. We were thus driven to the conclusion that each group represented an ion of at least some degree of stability. The fact that the opposite result was expected when the work was undertaken gives all the more value to the conclusion arrived at. The results of the phosphorus investigation are given in column G; the groups given there were observed when dried air as well as undried air was passed over phosphorus. The phosphorus observations supported the previous conclusion that the mobilities were definite and did not change with time. The agreement between the mobility values gave still further confirmation of the group idea.

APPARATUS AND METHOD.

The work described in the present paper was commenced as soon as possible after the appearance of Blackwood's paper. As he had based his conclusion that there were no groups on results obtained with the Zeleny method, it was decided to use that method in trying to confirm our previous work. Blackwood examined the ionization produced by spraying water and also that formed when air is passed over a hot platinum wire. The writer has never investigated the ionization produced in the latter way but the experience of other workers in this laboratory is that it is difficult unless very special precautions are taken to obtain steady conditions when dealing with this type of ionization. The quantity of ionization obtained by bubbling air through alcohol or by passing air over phosphorus is much larger than that due to spraying water. Another important consideration is that in the water spraying experiments of J. J. Nolan, the results are not consistent in the region of the larger ions.[1] Variations are observed in the mobility values of two of the groups which are larger than would be expected from experimental errors. Two observations of a mobility which does not enter into the group system are recorded. Variations in the quantities of the different groups are noticed. This variation is especially noted in the largest ion and sometimes the quantity of this ion present is so small that it would be difficult to assert that it was not absent. These considerations led to the use of the alcohol and phosphorus methods of producing ionization in preference to the hot wire and water spray methods. This decision was also influenced by the fact that the writer is more familiar with the former methods.

The arrangements of the apparatus for bubbling air through alcohol and for passing air over phosphorus were essentially the same as those described in previous papers. The Zeleny method of measuring mobilities, as used by Blackwood, consists in drawing the ionized air through a tube containing two central electrodes separated by a short gap. The longer electrode is earthed and the shorter electrode, which is the farther from the entrance to the tube, is insulated and connected to an electrometer. Curves are drawn with the voltages on the outer tube as abscissæ and the currents to the short insulated terminal as ordinates. It is easy to show that if there are present ions of one mobility the curve will consist of one peak and that if several groups of ions are present there will be several peaks, one corresponding to each group.

Two Zeleny mobilities tubes were used during the course of the work; their dimensions are as follows:

[1] P. R. I. A., Vol. 33 (A), p. 17, 1916. P. R. S., Vol. 94, p. 126, 1917.

Internal diameter of outer tube (in both tubes)	= 3 cm.
External diameter of inner electrode (in both tubes)	= .95 cm.
Length of earthed electrode	37.4 and 10 cm.
L_1 length of insulated electrode	12.3 and 5 cm.
L length of earthed electrode + insulated electrode + gap	49.8 and 15.1 cm.

One tube was more than three times as long as the other and the ratio L/L_1 was approximately four in the long tube and three in the short tube. The tube which Blackwood used was nearly three times as long as the longer tube and his ratio L/L_1 was four. This ratio is important because the bigger it is the more pronounced should be the peaks on the Zeleny curve. On the other hand, the larger the ratio the smaller will be the quantity of ionization for measurement. The shortening of the insulated electrode introduces another very serious difficulty, the nature of which will be referred to later.

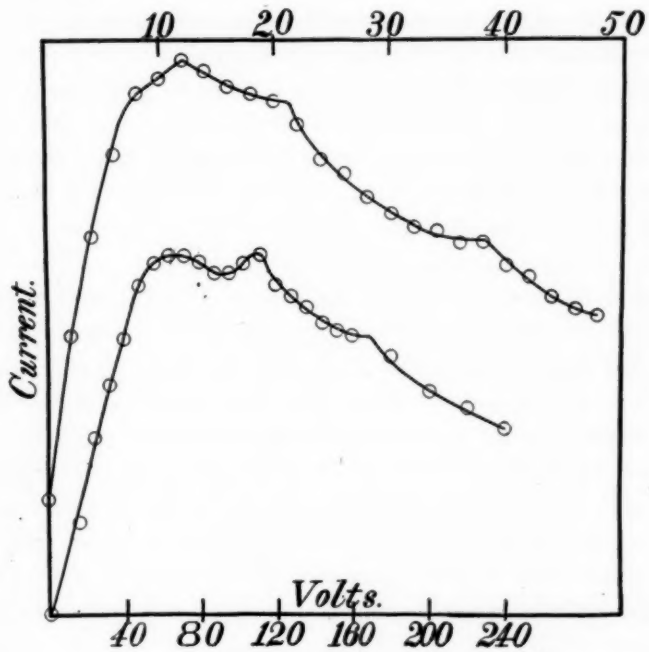

Fig. 1.

Results with Alcohol.

The ionization produced by bubbling air through alcohol was first tested using the long mobility tube. One of the first curves obtained is the upper curve given in Fig. 1. The voltages referring to this curve are shown along the upper horizontal line of the figure. In general outline it resembles the curves given by Blackwood. There is only one

peak but there are two decided corners at 21 and 38 volts and perhaps a corner at 7 volts. If voltage steps twice as large had been used these corners would scarcely have been detected and a smooth curve would have been the result. Although these corners show clearly that there is not a continuous spectrum of mobilities, there is a wide difference between this curve and the theoretical curve given by Blackwood, the realization of which experimentally he looked for as a confirmation of the existence of groups. This theoretical curve is that due to three groups of ions of mobilities in the ratio 1, 2.5 and 11 present in equal quantities and it shows three well-defined peaks. Our experience shows that the groups are present in varying proportions which seldom approach equality. If a theoretical curve were drawn with one group present in large quantity and others in smaller quantities, the peaks would not be so well marked. Again with alcohol and phosphorus the ratio of mobilities is 1, 1.8, 3.4, etc. The ratio of successive mobilities has a considerable influence on the appearance of the Zeleny curve; the closer the mobilities the less defined are the peaks. We have given reasons why the spray ionization was not used and we considered that these reasons outweighed the advantage that the spray ions are in general more widely spaced than the ions due to alcohol or phosphorus. Making allowance for the inequality in the amounts of the different groups and the closeness of successive mobilities a theoretical curve would be drawn with peaks not so well marked as in Blackwood's theoretical curve. These two considerations, however, are not sufficient in themselves to explain the non-appearance of peaks in this curve. An explanation may be found by consideration of the fact that the ions are changing while passing along the mobility tube. This will cause a rounding-off of the peaks and a filling-up of the hollows in the theoretical curve as ions which grow during their passage through the tube will appear to have mobilities which are between their initial and final values in the tube. It is obvious that if a very long mobility tube and a very slow air-blast were used the ions would spend a long time in the tube and the effect of change might be so great as to obliterate any evidence whatsoever of groups. Accordingly we can interpret the corners on the curve as peaks of the theoretical curve which are flattened and almost obscured by the growth of the ions in the tube. If this interpretation is correct the curve indicates the presence of three groups (and a possible fourth) the mobilities of which can be deduced by taking the voltages at the points of discontinuity as saturation voltages for the various groups. Furthermore it should be possible to obtain curves more like the theoretical curve by reducing the time which the ions spend in passing along the mobility tube. Experiments were accordingly con-

ducted with various air blasts faster than that used in the first experiments. Various volumes of tubing were inserted between the bubbling vessel and the mobility tube so that the time interval between the formation of the ions and the measurement of their mobilities might be equal to or in some cases greater than the time-interval used in the previous experiments. The longer this time-interval, the bigger will be the ions when they reach the tube and consequently the less will the ions change when passing along the tube. The time of the ions in the field can also be reduced by reducing the length of the tube and it was with this object that the shorter mobility tube was used in some experiments.

The lower curve in Fig. 1 was obtained using a faster blast than that used in the previous experiments. This curve shows two well marked humps and one corner. This curve is more like the theoretical curve; one peak is like the peaks in the theoretical curve but the other peak is much flatter. This curve places the existence of group of ions beyond any doubt. The two peaks are undoubtedly due to two distinct groups of ions and the corner indicates the presence of a third group.

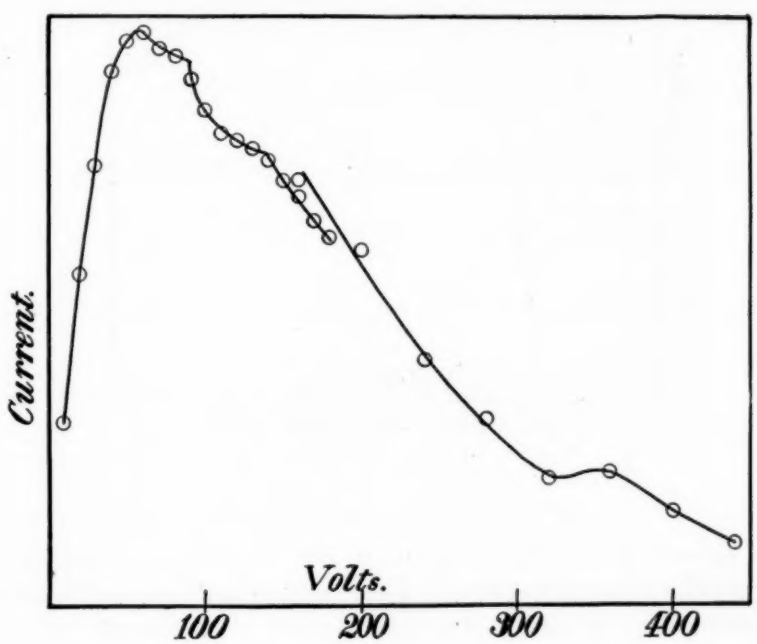

Fig. 2.

Fig. 2 gives another sample of the curves obtained with the alcohol ionization. Two parts are shown representing separate experiments in which the conditions were the same. In this curve there is a peak,

two corners and a hump at a high voltage. The hump at 360 volts is convincing evidence of the existence of a separate group of mobility approximately equal to .00067 cm./sec. A preliminary consideration of the theoretical Zeleny curve, taking into account the various causes which might obscure peaks, led to the conclusion that peaks would be more easily observed on the right hand side of the maximum point of the curve. This conclusion was justified by the results obtained during the course of the work.

To obtain still better definition of the peaks experiments were performed with faster blasts and with the shorter mobility tube. Results so obtained will be discussed later.

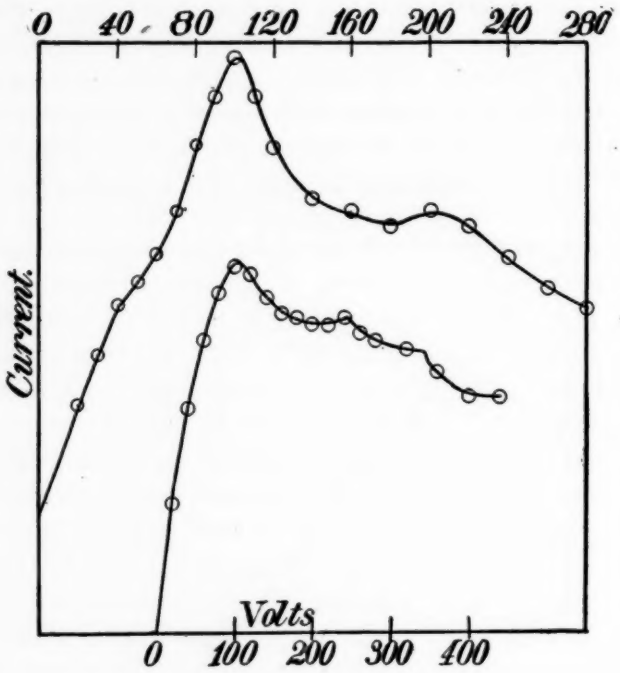

Fig. 3.

RESULTS WITH PHOSPHORUS.

The upper curve in Fig. 3 is due to the phosphorus ionization, the longer mobility tube being used. There are two well-marked peaks and one corner, showing clearly that groups exist in air passed over phosphorus. The lower curve in Fig. 3 gives another sample of the phosphorus curves; it shows the presence of three groups. Curve *A*, Fig. 4, is the only instance of a definite peak at a small voltage well removed from the maximum peak of the curve. It is plotted with the means of two series taken, one immediately after the other, which agreed very well. When

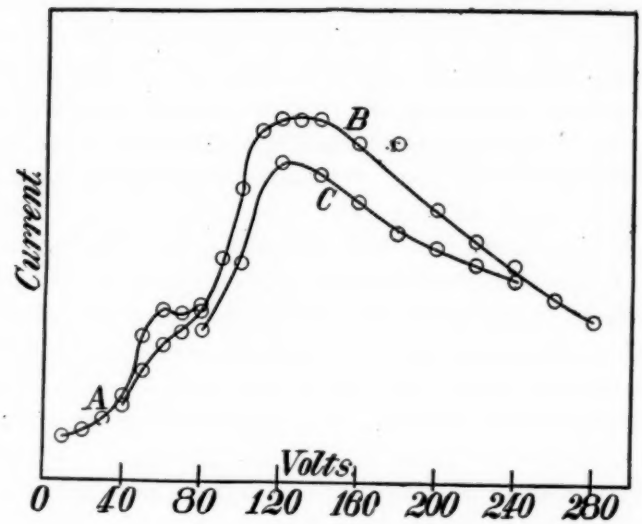
Current
A
B
C
D
Volts
0
40
80
120
160
200
240
280

Fig. 4.

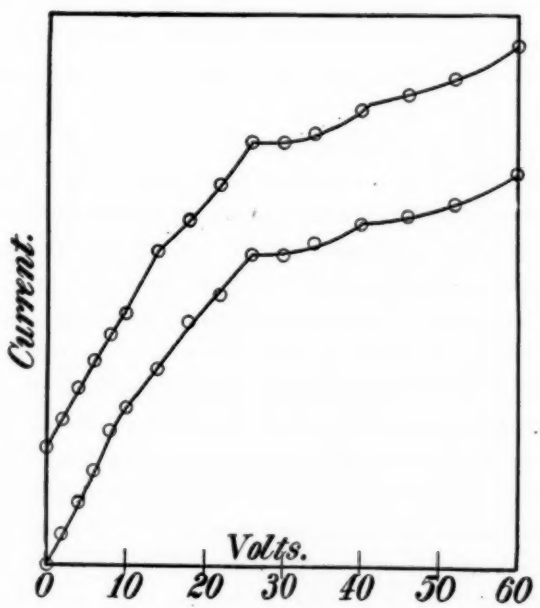
Current.
Volts.
0
10
20
30
40
50
60

Fig. 5.

the complete curve *B* was taken this peak at 60 volts had become flattened out but there still remained evidence of a group at this point. Curve *C* taken immediately after Curve *B* gives the same mobility for its highest point but its peak is sharper. It is an interesting fact that the sharpness of the peaks varies considerably and in this case the variation occurs during an immediate repetition of the numbers. In the previous paper on phosphorus changes in the nature of the ionization were recorded and also the fact that some of the groups of ions could not be observed on some occasions. The three curves in Fig. 4 also show a variation in the quantity of the ionization. This variation was often noticed when observations were repeated both in the case of the phosphorus and alcohol but it is thought that such variations do not affect the validity of the arguments from the whole series of curves. It may be noticed that the number for 180 volts in curve *B* is well above the curve. A peak is not drawn here because it would depend on only one number and it does not appear in curve *C*. The peaks and corners on which we rely depend on current observations for several successive voltages and are supported by other curves. A slight continuous variation of the quantity of ionization during an experiment such as sometimes occurred does not affect the general evidence of the curves. It may be remarked here that in the previous work by the McClelland method practically all the curves were drawn using the means of observations with ascending and descending voltages. As in those experiments a short part of the curve was examined, the experiment was performed in a short time and the variations which occurred during a series of observations were small.

Fig. 5 gives portion of a curve worked over in detail using the smaller mobility tube. One curve was taken immediately after the other. The difference between the two sets of numbers is very small. The curves are plotted apart with different zeros but as the zero for both curves is given it will be seen how good is the agreement between the readings for the various voltages. There is a well marked corner at 26 volts and a faint corner about 40 volts in both cases. It is interesting that the corner at 26 volts is so well marked as the mobility deduced from it (.033) cannot be fitted into the groups we have already found. There is some evidence of corners about 8 volts in one curve and about 14 volts in the other curve. However as this region was not fully explored there is no further evidence for or against groups at these points. A slight difference in the numbers about this region in the two curves causes the appearance of the corner at 8 volts in the one case and at 14 volts in the other. This lack of agreement also prevents us from making any decision.

This completes a selection of the curves obtained. In all about thirty curves were taken and only two of these curves showed no evidence of a peak or corner in addition to the main peak. The failure to obtain evidence of groups on these two occasions can be explained. One of these curves was taken with a slow blast and this as we have seen militates against the observation of groups. In the other curve only two numbers were taken on the left hand side of the maximum point of the curve and possibly a corner there escaped notice.

Intermediate Mobilities.

During the course of the alcohol investigations an attempt was made to get if possible even better defined peaks by shortening the time of the ions in the mobility tube. Fast air-blasts were used and the shorter mobility tube was also used with this object. The curves obtained did not show better defined peaks but they indicated the presence of some groups of intermediate mobilities. The mobilities calculated from the previous experiments agreed fairly well with the numbers set forth in Table I. The curves now obtained showed not only these mobilities but indicated that some groups of mobilities of intermediate values were present. This matter was not fully investigated and all that can be said at present is that indications of such intermediate groups were noticed. These groups may merely represent stages in the process of growth of the ions or in other words less stable aggregations which persist for a short time in the growth between two more stable ions. The percentage of such ions present will be smaller than the percentage of the more stable ions and consequently a good resolving method is necessary for their discovery. This agrees with the fact that indications of their presence were obtained when using the Zeleny method in the manner in which one might expect the best definition of peaks. The presence of such groups would explain why the main peaks were not better defined in previous experiments and might also account for the variation in the width of the peaks.

Agreement with Previous Results.

The general agreement between the mobility values obtained by the Zeleny method and those obtained by the McClelland method is shown in Table II. The present numbers are not so numerous or exhaustive as the previous ones. Mobilities of intermediate groups are not included.

TABLE II.

Al. (McC.)	.049		.017	.0077	.0040	.0023	.0014	.00063	.00034
Ph. (McC.)	.053	.028	.018	.0074	.0041	.0024	.0012	.00064	.00031
Al. (Ze.)	.049	.025	.018	.0075	.0045	.0026	.0014	.00067	
Ph. (Ze.)		.022		.0075	.0043	.0026	.0014	.00074	.00035

BLACKWOOD'S RESULTS.

It is possible to explain fairly satisfactorily the difference between the results obtained by the writer with the Zeleny apparatus and Blackwood's results with the same type of apparatus. We have already emphasized the importance of the length of time spent by the ions in the mobility tube and it is interesting to compare the researches in this respect. If we divide the volume of the tube by the volume of the blast per second we get the average time of the ions in the tube. The volume of the tube $= \pi(b^2 - a^2)L$, where b is the internal diameter of the outside tube, a is the external diameter of the electrode and L is the sum of the lengths of the earthed and insulated terminals and the small gap between them. In Blackwood's apparatus $L = 140$ cm. and the cross-section = 16.5 sq. cm.; in the author's apparatus $L = 49.8$ cm. and the cross-section = 6.4 sq. cm. The corresponding volumes are 2310 c.c. and 320 c.c. approx. Thus for the same air-blast the time of the ions in the tube was seven times longer in Blackwood's experiments than in ours.

From the summary of Blackwood's paper published in the Proceedings of the Nat. Acad. of Sciences, May, 1920, we see that in the experiment there quoted the ions of mobility .0004 cm. per sec. would be saturated at about 40 volts. This enables us to calculate the air-blast and we thus deduce that in this experiment the ions spent about 150 seconds in the mobility tube. Similarly from the curves given in Fig. 11 of Blackwood's paper in the PHYSICAL REVIEW it can be calculated that the corresponding time in the experiments with the hot wire was about 9 seconds. These experiments were conducted for the purpose of examining the relation between the mobility and the age of the ions and were apparently carried out with the fastest air-blast used. Thus it seems probable that the extreme values of the time of the ions in the tube were 150 and 9 seconds. In our work the extreme values for this time were 13 and .5 second. The times in our experiments were much shorter than Blackwood's and we think that this to a large extent explains why he failed to detect groups. It is possible that if he used smaller voltage-steps, especially in the experiments conducted with fast air-blasts, some discontinuities might have been observed. If intermediate groups are present even in small quantities they would have an obscuring effect on the peaks of the

Zeleny curve. Possibly this is a contributory cause of Blackwood's failure.

In examining spray ions by the McClelland method, Blackwood obtained curves showing breaks, indicating a ratio of about 2 for successive mobilities. Table I. shows that J. J. Nolan found the spray ions had a ratio of about 3.4 between successive mobilities. The ratio in the case of the phosphorus and alcohol ions is about 1.8. It is possible that in Blackwood's experiments the ions of mobilities such as .00064, .0023, .0075, etc., were present just as in the case of alcohol and phosphorus. (J. J. Nolan observed the group of mobility .00064 sometimes.) This would account for the ratio observed. We have never properly understood why there should be twice as many groups in ionization due to alcohol or phosphorus as in that due to water or mercury. It may be connected with the relative quantities of positive and negative ions. In the case of alcohol and phosphorus the number of ions of the two signs are always exactly equal; with water and mercury this is not so.

McClelland Method.

It is interesting in the light of the new information about the growth of the ions and the possible existence of intermediate groups to discuss the previous results obtained with the McClelland method. Blackwood shows that the Zeleny method is much better than the McClelland as a detector and resolver of group ionization. The question then arises as to how the groups were obtained with the McClelland method and not with the Zeleny method as used by Blackwood. Comparison of the length of the time which the ions spent in the tube explains this to some extent; in previous work with the McClelland method that time-interval was generally of the same order as that used in the present work and was thus smaller than the time in Blackwood's experiments. But there is another important consideration which shows that the flattening out of the theoretical curve due to the growth of the ions is much more serious in the Zeleny method than in the McClelland method. The ions captured in the insulated terminal of the Zeleny tube are those which have moved along the greater part of the tube; in the McClelland method ions begin to be captured on the insulated terminal at the moment of their entry into the field. Hence the effect of change of the ions is smaller in the McClelland than in the Zeleny tube; the larger the ratio between the earthed and the insulated electrodes of the Zeleny tube, the greater will be the effect of growth.

If intermediate groups exist it is not surprising that they were not detected by the McClelland method. They are probably present in

small quantities and the McClelland method was not able to resolve them from groups nearly equal in mobility present in large quantities. It was only when the Zeleny method was being used in a highly resolving manner that indications of these intermediate groups were noticed.

CONCLUSION.

The results obtained in the present work place beyond doubt the existence of homogeneous groups of large ions. The curves admit of no other explanation. The numerical agreement between the mobility values of the different groups deduced from the Zeleny curves and from the McClelland curves shows that both types of curves have been correctly interpreted. The present paper suggests the reasons for Blackwood's failure to find any evidence of groups. Furthermore, it shows how it was possible to detect and examine groups of ions in the previous work although it was carried out by a method of admittedly inferior resolving power.

The results of the present paper do not enable us to add to the hypothesis put forward by J. J. Nolan to account for the production of different classes of ions. It seems likely that further knowledge of the nature of this ionization will be obtained more readily by attacking the question from a different angle rather than by continuing work on the present lines.

The author wishes to express his indebtedness to his brother, Professor J. J. Nolan, for his help and advice during the course of this research.

UNIVERSITY COLLEGE, DUBLIN,
March, 1921.

THERMOELECTRIC ELECTRIC EFFECTS IN IRON AND MERCURY DUE TO ASYMMETRIC HEATING.

By J. M. Benade.

Synopsis.

Thermo-electric Effect Due to Temperature Gradient Along a Constriction.—(1) *Iron rod.* Using constrictions from 0.5 to 4 mm. in diameter and from 0.5 to 1.5 mm. in length, electromotive forces were obtained with gradients of a few degrees per mm. large enough to be measured easily with a sensitive galvanometer. For each constriction the effect was found to be proportional to the temperature gradient. The fact that it decreased as the mean temperature was increased indicates that it is not an inverse Thomson effect. Moreover it depends on the dimensions of the constriction, being less for the smaller diameters. (2) *Mercury.* By using two relatively large quantities of mercury connected through a pin hole in an intervening sheet of mica, a temperature gradient of at least 600° C. per m.m. could be maintained in the constriction, but a high sensitivity galvanometer failed to indicate any electromotive force although according to Benedick's conclusions[1] a deflection of over 50 divisions should have been observed. His results are explained as due to a true thermo-electric effect between the mercury and the slate tube containing it. (3) *In explanation* it is suggested that the effect is associated with the non-homogeneity produced by the mechanical stresses set up in the iron as a result of unequal thermal expansion and is not due merely to the flow of heat through the constriction.

IT has been generally assumed that the e.m.f. produced by the asymmetric heating of conductors is an inverse Thomson thermoelectric effect. It was on this assumption that an attempt was made to measure the temperature coefficient of the Thomson effect by observing the rate of change of this thermo-e.m.f. with a change of mean temperature of a constriction in various metals, the temperature gradient in the constriction being maintained constant. With this object in view various forms of apparatus were used, the one shown in Fig. 1 being typical. The temperature gradient in the constriction as well as the absolute temperature was controlled by means of heating coils. The temperatures were measured by means of the usual copper constantan thermo couples, which it was found necessary to insulate carefully from the rod into which they were inserted. To the ends of the rod were soldered iron wires and to these in turn copper wires which were connected to a high sensitivity galvanometer. In order to prevent spurious thermoelectric effects both pairs of junctions were kept in constant temperature baths.

The thermo-junctions protected by thin-walled glass capillary tubes were inserted into holes 1.5 mm. in diameter in the iron rod on opposite

[1] Comptes Rendus, 169, No. 13, Sept. 29, 1919.

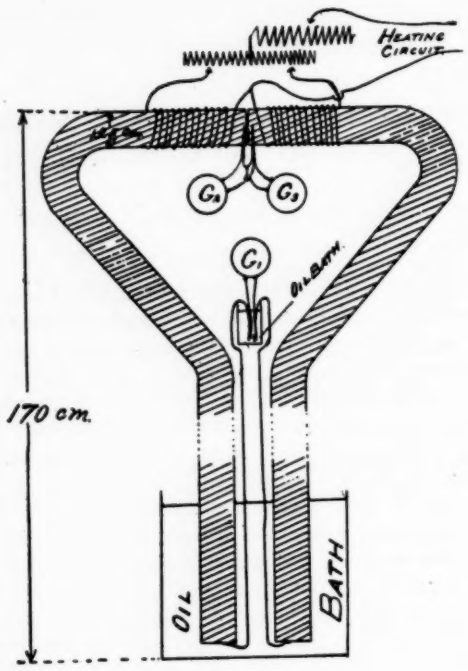
HEATING CIRCUIT
G_2
G_3
C_1
OIL BATH
170 cm.
OIL
BATH

Fig. 1.

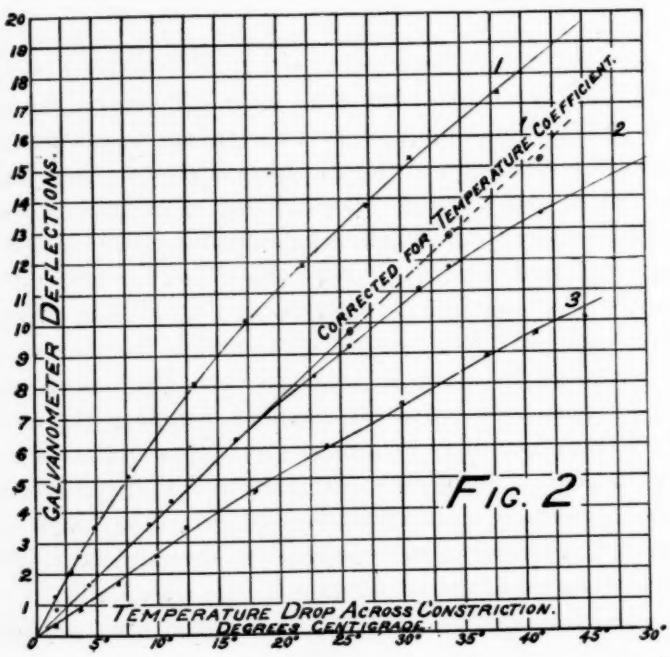
GALVANOMETER DEFLECTIONS.
TEMPERATURE DROP ACROSS CONSTRICTION.
DEGREES CENTIGRADE.
CORRECTED FOR TEMPERATURE COEFFICIENT.
1
2
3
FIG. 2

Fig. 2.

sides of the constriction with a distance of about 4 mm. between their centers. The constrictions varied from 4 mm. to 0.5 mm. in diameter and from 1.5 mm. to 0.5 mm. in length. It was found that for very sharp constrictions with correspondingly abrupt temperature gradients, for a given difference of temperature between the ends of the constrictions relatively small e.m.f.'s were obtained. The greatest effects were obtained when the constrictions were not very deep, though this point has not been carefully investigated. The important fact for our present purpose is that the e.m.f. is found to depend not merely upon asymmetry in the temperature gradient but also upon the dimensions of the constriction. This is shown by the curves in Fig. 2, and in Fig. 3.

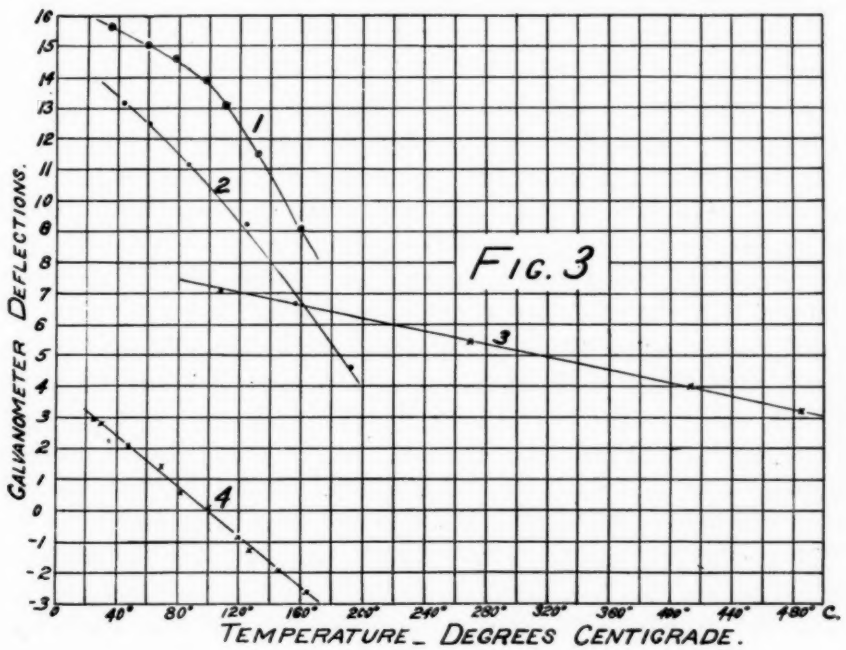

Fig. 3.

The curves in Fig. 2 show the relation between the e.m.f. and the temperature gradient in the constriction. Were it not for the fact that the mean temperature of the constriction during each run was constantly rising, the curves would have been rectilinear, for, as will be later shown the temperature coefficient of the effect is negative. In other words the e.m.f. for a particular apparatus is directly proportional to the temperature gradient in the constriction. It is assumed always that the only asymmetry in the temperature gradient is at the constriction. Small errors are actually introduced because this is not always strictly true,

though in general these errors are negligible. Curves 1, 2 and 3 were obtained under similar conditions except that the constriction was reduced after getting the data for the first, and again after the readings for the second curve, the third curve corresponding to the sharpest constriction. These curves show clearly that for given differences in temperature between the ends of the constriction the e.m.f. actually decreases as the abruptness of the temperature gradient increases.

In order to measure the temperature coefficient of the effect for any particular form of apparatus, the e.m.f.'s corresponding to mean temperatures of the constriction in which the temperature gradient was maintained constant, were observed. For this purpose a temperature difference between the ends of the constriction of about 20° C. was sufficient to produce convenient galvanometer deflections. In Fig. 3 are several typical curves representing the variation of the e.m.f. with the mean temperature of the constriction. The curves show that in each case the temperature coefficient is negative,[1] *i.e.*, the e.m.f. produced by a constant temperature gradient in the constriction decreases as the temperature rises. The value of this coefficient is found to depend upon the size and form of the constriction as well as upon the material concerned. The variations in the degree of slope and especially the direction of slope show definitely that the effect is not simply an inverse Thomson effect, for in that case the slope should be the same in all cases and should show a positive temperature coefficient as found by Berg,[2] and others. It seems probable that the effect is due to mechanical stresses set up in the iron by unequal thermal expansion which in some way alter the structure of the metal in or near the constriction sufficiently to give rise to the observed thermoelectric effects, as has been repeatedly suggested.

The unexpected results above recorded indicated that the observed e.m.f.'s are due to a lack of homogeneity in the asymmetrically heated conductor. The crucial test for the existence of the effect is its detection in the case of mercury. Benedicks[3] claims to have observed and measured the effect in mercury though Haga and Zernike[4] using a very much better form of apparatus conclude that there is no true effect due merely to asymmetric heating of the conductor. Repeated attempts with various forms of apparatus were made but with negative results in each case though an effect of the same order of magnitude as that obtained in iron should have been very easily obtained. A diagram of the final form

[1] Curve No. 4 which indicates a reversal of the effect is rather less reliable than the others though there is no reason to believe that it is not correct. The apparatus was broken before getting other readings.

[2] Annalen der Physik, Vol. 32, 1910, p. 477; Vol. 33, p. 1195.

[3] Comptes Rendus, 169, No. 13, Sept. 29, 1919.

[4] K. Akad. Amsterdam, Proc., XXI 10, p. 1262, 1919.

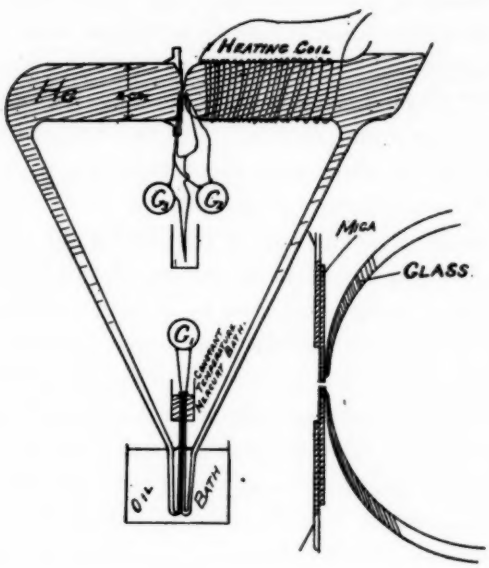

Fig. 4.

of apparatus used is shown in Fig. 4. The relatively large quantity of mercury used was contained in two tubes connected together by means of a pin-hole 0.35 mm. in diameter through an intervening sheet of mica 0.3 mm. in thickness. For the galvanometer connections smaller glass tubes were sealed on to the larger ones and suitably drawn out so that the necessary junctions with the galvanometer lead wires could be kept at exactly equal temperatures by means of a cup of mercury, in order to avoid all spurious thermoelectric effects. Differences in temperature on opposite sides of the constriction were measured by means of thermocouples encased in very fine capillary tubes. The galvanometer used gave deflections of one scale division per 10^{-8} volt, which though not so sensitive as the one used by Benedicks was sufficiently sensitive for the purpose. With this arrangement it was quite possible to keep the mercury on one side of the constriction at or below room temperature indefinitely while the mercury on the other side was slowly boiling. Though it was of course not possible to determine accurately the temperature gradient in the constriction it must have been not less than 600° C. per mm. and was probably nearly if not quite 1000° C. per mm. when the temperature difference between the two sides of the mica was 330° C. or more. Special care was taken in constructing the apparatus to reduce to the minimum conduction of heat from one side to the other through the glass and mica and at the same time to make full use of

convection currents in the mercury. The only deflections obtained amounted to four or five scale divisions and these were found to be due entirely to leakage from the heating circuit. Had there been an effect of the magnitude affirmed by Benedicks a deflection of at least 50 scale divisions should have been obtained, for the temperature gradient in the present experiment must have been very much greater than it is possible to obtain in small glass or slate tubes.

If there were in mercury an effect of the same type as that obtained by the asymmetric heating of solid conductors the order of magnitude of the effect would probably be the same as in iron, in which case a drop of 0.005° C. in the constriction should have produced an appreciable deflection, though an actual drop of more than 330° C. produced no observable effect. Since it has been suggested that an e.m.f. may be produced by the rapid conduction of heat across a constriction a modification of the above described apparatus was made in order to test this hypothesis. As described the apparatus was designed to reduce heat conduction to a minimum so that if this were the true explanation of the effect at most only a small effect would have been obtained. The pin-hole in the mica separating the two sections was enlarged to a diameter of about 2 mm. With this arrangement heat was rapidly conducted through the constriction though as before there was absolutely no indication of the existence of any e.m.f. in the circuit.

In explanation of the results obtained by Benedicks and of his cubic relationship, *i.e.*, that the e.m.f. produced in mercury when heated on one side of a constriction in a tube is proportional to the cube of the temperature drop in the constriction, it is suggested that the effect measured was due entirely to a true thermo-e.m.f. produced by the mercury and slate, the abnormal rate of increase being caused by the change in the conductivity of the slate containing-tubes. The thermo-e.m.f. produced by the slate mercury couple with 300° C. difference in temperature between the junctions is very large indeed in comparison with the quantities measured and the conductivity of slate is not extremely low, so that even though the mercury column was continuous the relatively small e.m.f.'s observed may thus be fully accounted for If this be the correct explanation it is to be expected that the effects in glass will be smaller. The apparatus described above should be nearly if not entirely free from the possibility of disturbances of this nature.

Results.—It seems to be definitely shown that if there be any true thermoelectric effect in mercury due to asymmetric heating it must amount to less than 10^{-8} volt for a gradient of 600° C. per mm. Also that if there be any effect due to a flow of heat it must be extremely small.

The effect in the case of iron and presumably of other metals is not an inverse Thomson effect. Since there is no effect in mercury to compare with that observed in solids it may be assumed that non-uniform temperature gradients in solids sufficiently disturb the homogeneity of the material to give rise to the observed e.m.f.'s and that these effects are not due simply to a flow of heat across a constriction.

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NOTE ON THE DYNAMICS OF CAPILLARY FLOW.

BY WILLARD GARDNER.

SYNOPSIS.

Theory of the movement of moisture in soil.—Attention is called to experimental data which show that there usually exist in the soil appreciable moisture gradients which indicate that it cannot be regarded as a bundle of capillary tubes and that therefore *Washburn's theory of capillary flow* does not rigorously apply in this case. However by using Poiseuille's equation modified by the assumption that the variation of moisture content does not appreciably change the kinematical resisting force, together with empirical equations derived from soil moisture studies connecting the capillary pressure and vapor pressure with the moisture content, an *equation for horizontal flow* is derived, $V = k(1 - e^{-\beta t})$, which is in qualitative agreement with experimental results. A more extended treatment of the subject is given in an article by the author in Soil Science.

IN the March number of the PHYSICAL REVIEW there appears an article by Washburn on "The Dynamics of Capillary Flow." In part 7 of this article he discusses the rate of penetration of a porous body by a liquid, arriving at a tentative relation:

$$V = k' \left(\frac{\gamma}{\eta}\right)^{1/2} t^{1/2},$$

where V expresses the volume of liquid absorbed, t the time, γ the surface tension, η the coefficient of viscosity, and k' a constant. He finds, however, that for large values of V this relation does not hold in the case of the absorption of water by charcoal.

In this connection, it may be of interest to note that a considerable amount of data are available from soils literature[1] showing that the volume of water absorbed by a soil is not always proportional to the pore space, as his equation (15), viz.,

$$V = \pi r^2 l$$

would indicate. On the other hand, the liquid "density" ρ (*i.e.*, the mass of liquid per aggregate unit volume of soil) is a function of the distance x from the source. Uniformity of soil moisture content is exceptional, whereas moisture gradients are frequently observed in moisture studies, although their magnitudes are usually small except at the im-

[1] See, for example, "Soils," by Hilgard, p. 209; "Physics of Agriculture," by King, p. 134; "Studies of the Movement of Soil Moisture," by Buckingham, *in* U. S. Dept. of Agr. Bur. of Soils Bul. 38; also "The Movement of Soil Moisture" by Gardner and Widtsoe, *in* Soil Science, Vol. XI., No. 3, March, 1921, Fig. 3, p. 224.

mediate water front where an abrupt change is often observed. This fact would seem to invalidate also the application of Washburn's equation (8) wherein he has made use of the reciprocal of r (*i.e.*, the radius of the equivalent cylindrical tube) as a measure of the curvature of the liquid surface. It is clear of course that his equations have been derived on the assumption that the porous body should approximate in character a bundle of capillary tubes and an attempt to apply the equations to a mass of soil is perhaps somewhat beyond his expectations. If, however, we regard the curvature factor of his equations (8) and (9) as a function of the liquid "density," which in turn depends upon the distance x from the source, these equations will apply provided Poiseuille's equation holds for this case.

In the March number of *Soil Science* the writer has made use of Poiseuille's equation modified for variable "density" by introducing the assumption that the kinematical resisting force is independent of the "density." Or, what amounts to the same thing, that the average velocity v of the moisture is proportional to the pressure gradient and independent of the moisture content,

$$v = K_1 \nabla p. \tag{1}$$

The capillary pressure p is determined by the curvature of the air-water surface and this in turn is determined by the moisture content. Due to the complexity of this surface configuration, however, we are forced for the present to rely upon experiment for this functional relation. The experimental data of Briggs[1] on the moisture content as a function of the reciprocal of the "centrifugal" force to which the moist soil is subjected leads to an equation which holds over a wide range of moisture contents of the form,

$$p = \frac{c}{\rho} + b. \tag{2}$$

This involves the assumption that the capillary pressure is proportional to the equilibrium "centrifugal" force. Thomas's[2] vapor pressure measurements for varying moisture content lead also to an equation of the form,

$$\pi = \pi_0 - \frac{c_1}{\rho}, \tag{3}$$

where π is the vapor pressure and c_1 is a small constant, this equation representing the experimental facts over a considerable range of moisture contents.

[1] U. S. Dept. of Agr. Bur. of Soils, Bul. 45.

[2] Soil Science, Vol. XI., No. 6, June, 1921.

By a familiar method it may be shown that the vapor pressure and the capillary pressure are related as follows:

$$p = \pi - nRTln\frac{\pi}{\pi_0} \tag{4}$$

and a simple algebraic substitution leads to a converging series which, for finite values of π differing only slightly from the average vapor pressure π_0 of water, gives a relation also of the form,

$$p = \frac{c_2}{\rho} + b, \tag{5}$$

from which,

$$\nabla p = \frac{c_2}{\rho}\nabla\rho. \tag{5'}$$

Combining (1) and (5'), we obtain,

$$v = K_2\frac{\nabla\rho}{\rho}. \tag{6}$$

And combining equation (6) with the equation of continuity,

$$\frac{\partial\rho}{\partial t} = -K_3\nabla(\rho v) \tag{7}$$

we obtain,

$$\frac{\partial\rho}{\partial t} = -K_4\nabla^2\rho. \tag{8}$$

From (8), we may obtain a solution of the form,

$$\nabla\rho = K_5 l^{-\alpha x} l^{-\beta t}. \tag{9}$$

From equation (9), equation (6) may be reduced, for one-dimensional flow, to the following form,

$$v_l = \frac{dl}{dt} = \frac{K_2 l^{-\alpha x} l^{-\beta t}}{\rho_l} \tag{10}$$

where l is the coördinate of the water front, α and β are constants. If α (which is a measure of the moisture gradient) is small, ρ_l and the factor $K_2 l^{-\alpha x}$ remain practically constant, giving an equation of the form,

$$\frac{dl}{dt} = K_6 l^{-\beta t}, \tag{11}$$

which becomes when integrated

$$l = K_6(1 - e^{-\beta t}) \tag{12}$$

and the approximate value of V

$$V = K_7(1 - e^{-\beta t}), \tag{13}$$

which is in qualitative conformity with the experimental data of Cude and Hulett as quoted by Washburn. Equation (8) and a somewhat more general equation taking account of gravitational and hydrostatic potentials have been solved for special cases with qualitative experimental confirmation, as reported more in detail in the article noted.

It is true, of course, that these equations rest upon empirical data, together with the assumption which has been made with reference to the application of Poseuille's equation, but a considerable amount of material has been presented in the article cited indicating that they are not far from correct.

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THE CRYSTALLINE STRUCTURES OF SPUTTERED AND EVAPORATED METALLIC FILMS.[1]

BY H. KAHLER.

SYNOPSIS.

Crystalline structures of evaporated films of bismuth and silver, condensed on a cool surface, were determined by the X-ray powder method. The films were found to contain no pure metal in the crystalline state, but to consist of amorphous metal and of metallic compounds. Optical evidence indicates that *selenium* also condenses on a cool surface in the amorphous form, although on a heated surface crystals are deposited whose size and color depend on the temperature.

Crystalline structures of sputtered films of bismuth, cobalt, gold, platinum and silver, as determined by X-ray analysis, were in each case the same as that of the unsputtered metal. The crystal grains had a random distribution of axial direction. Evidently in sputtering crystalline grains are knocked off the cathode and are transported and deposited grain by grain, whereas evaporation takes place atom by atom.

Relative sputtering of hexagonal and cubic forms of cobalt. The hexagonal form is easily sputtered whereas the other form is not.

Crystalline structure of bismuth, determined by X-ray analysis of the powdered metal and sputtered film, is rhombohedral trigonal, with elementary triangular prism of side 4.54 Å and height 5.91 Å.

INTRODUCTION.

THE optical and electrical constants of thin metallic sputtered and evaporated films have been the subject of investigation for many workers since the pioneer experiments of Plücker. The crystallographic study of such films, however, has never been undertaken. As a result of the conductivity experiments[2] by Professor Richtmyer, Mr. J. A. Becker and Mr. L. F. Curtiss on sputtered films of bismuth it was questioned by the latter whether their films were crystalline. It was in part to answer this question that the writer's experiments were originally undertaken.

Method.

The x-ray powder method as developed in Germany by Debye and Scherrer[3] and in America by Hull[4] was used in this study. As a source of Rontgen radiation a small General Electric molybdenum-target x-ray

[1] An abstract of this paper was read before the Chicago section of the American Physical Society, Dec., 1920. PHYS. REV., 17, p. 230, 1921.

[2] J. Becker and L. Curtiss, PHYS. REV., 15, p. 457, 1920. F. Richtmyer and L. Curtiss, PHYS. REV., 15, p. 465, 1920.

[3] P. Debye and P. Scherrer, Phys. Zeits., 17, p. 277, 1916; 18, p. 291, 1917.

[4] A. Hull, PHYS. REV., 10, p. 661, 1917.

tube which normally operates on two milliamperes current and 30 kilovolts potential was used. The photographic films consisted of two thicknesses of duplitized material which were clamped half way around two rigidly fastened metal rings turned on a lathe to an exact circle of 17 cm. diameter. One ring was supported about two centimeters vertically above the other by means of iron straps. The powdered material to be examined was in the form of a flat sheet and was put at the center of the circular films. A filter of zirconium oxide of thickness four tenths of a millimeter was inserted in the path of the x-rays between the tube and the lead slits used in defining the beam. The slits were each about a half millimeter wide. The slits, powder and circular photographic films were enclosed in a heavy lead box to screen off stray radiations.

Intensifying screens were discarded after a few tests as they were found of little value for a tube of low power output.

Bijl[1] has pointed out that under some conditions a large correction must be applied to the calculation of the planar spacings. This correction was avoided in the present work by using a layer of crystalline powder of such small thickness that it was easily penetrated by the x-rays.

STRUCTURE OF BISMUTH METAL.

Filings from a rod of bismuth were sifted through a screen 100 mesh to the centimeter, mixed with a small amount of soft wax, pressed into a flat sheet and put at the center of the circular photographic films. Exposures of 150 milliampere hours were made.

Knowing the crystal system and axial ratio from the standard crystallographic works, tables of planar spacings could be computed. It was found that the lattice may be considered as being made up of three interpenetrating sets of unit equilateral-triangular prisms, the atoms of the second set being raised one third the prism height vertically above the first and placed so that their vertical projections center alternate triangles of the basal plane. The third set are raised two thirds of the prism height above the first set, and center the remaining alternate triangles. The experimental values were in agreement with the theoretical values for the rhombohedral trigonal structure with elementary triangular prism of side 4.54 A and height 5.91 A with an axial ratio of $C = 1.303$.

Beyond the first eight lines the intensities were too faint to place with certainty the weaker experimental lines.

[1] A. Bijl and N. Kolkmeyer, Proc. Amst. Acad., 21, 1, p. 495, 1918–1919.

TABLE I.

Indices.	Theor. Spacing.	Exp. Spacing.	Intens.	No. of Planes.
$10\bar{1}1$	3.27	3.28	V. Strong	3
$10\bar{1}2$	2.36	2.38	V. Strong	3
$11\bar{2}0$	2.27	2.25	V. Strong	3
0001	1.97	1.96	V. Weak	1
$20\bar{2}1$	1.84	1.83	Weak	3
$10\bar{1}1$	1.64	1.64	Medium	3
$11\bar{2}3$	1.49	1.50	Strong	6
$21\bar{3}1$	1.44	1.44	Strong	6
$10\bar{1}4$	1.38	——	——	3
$12\bar{3}2$	1.33	1.33	Strong	6
$10\bar{1}0$	1.31	——	——	3
$10\bar{1}2$	1.18	——	——	3
$10\bar{1}5$	1.14	1.15	V. Weak	3

For a check the number of atoms for the three interpenetrating unit prisms, in this case 1.5 may be computed;[1]

$$n = \frac{52.8 \times 9.7}{1.663 \times 208} = 1.49.$$

SPUTTERED BISMUTH.

Pure cast bismuth was used as a cathode in the sputtering jar. The current used was about one milliampere, the jar being in series with a kenetron rectifying-tube. The time of sputtering was about four hours. The bismuth was sputtered on several thin cover glass slides. When these slides with their metallic films, were superposed and put at the center of the photographic films the result was striking. The positions and intensities of the lines were nearly identical with those obtained with the bismuth rod filings, the only difference being a greater fogging of the lines. This fogging and lack of definiteness is due to the presence of small amounts of oxides of bismuth and to amorphous material.

The conclusion to be drawn from this comparison is that sputtered bismuth is crystalline, the crystal axes being turned in all possible directions, and the structure being the same as the ordinary metal. Although compounds of bismuth with the gases in the sputtering jar were undoubtedly present in small quantities, the pure metal was so predominant as to mask the spectra of the impurities.

EVAPORATED BISMUTH.

A piece of bismuth was put in the bottom of a long pyrex tube and the tube evacuated to approximately the same pressure as was used in sput-

[1] A. Hull, PHYS. REV., 10, p. 661, 1917.

tering the bismuth. On heating the bottom of the tube till the bismuth came to a low red heat a heavy opaque film was deposited on the cooler parts of the tube. This film was examined by the method previously described. The photograph showed four widely spaced lines on a heavily fogged background indicating the absence of bismuth crystals but probably the presence of amorphous bismuth and a bismuth compound which however could not be identified.

A second sample of evaporated bismuth was prepared. The film was scraped from the glass, mixed with wax as in previous experiments and pressed into a flat sheet. When this was exposed to the x-rays in the usual manner the result was the same as that described above.

This would indicate that sputtering and evaporation are essentially different processes from the crystallographic standpoint.

The Structure of Sputtered Gold, Silver and Platinum.

In a similar manner the structures of sputtered films[1] of gold, silver and platinum were determined. In each case the sputtered film was crystalline and of the same fundamental crystal structure as the ordinary metal. The three metals have the face-centered cubic lattice with the length of the elementary cube 4.08, 4.06 and 4.02 Å respectively. The crystals are very minute and have a random distribution of axial directions.

Evaporated Silver.

Several opaque layers of silver were prepared by evaporation from an electrically heated silver wire in an evacuated vessel. These films were deposited on strips of lime glass. On examination they were found to be without the typical silver structure. The photographs were taken within one day after making the silver film.

In this connection it is interesting to note that Hull has found that distilled sodium and potassium are amorphous.[2] It is obvious beforehand that rapid evaporation in vacuo to a cold surface offers a favorable opportunity for the formation of a metal in the amorphous state.

Sputtered Cobalt.

This metal[3] occurs in two systems, the face centered cubic and the close-packed hexagonal, the former of which is made by annealing in a hydrogen furnace while the latter is made by rapid electrolysis.

The electrolytic cobalt sputtered readily and the structure of the film obtained from it was hexagonal.

[1] The films of gold and silver were sputtered by Mr. L. Koller.

[2] A. Hull, Phys. Rev., 10, p. 688, 1917.

[3] A. Hull, Trans. Am. Inst. El. Eng., 38, p. 1189, 1919; Phys. Rev., 17, p. 571, 1921.

On the other hand, samples of cobalt consisting largely of the cubic variety did not sputter at all under the same conditions as obtained in the case of the hexagonal variety.

This indicates that rapidity of sputtering is determined in some cases by the crystal structure of the cathode. In the case of cobalt the less stable hexagonal arrangement seems to sputter better than the stable cubic variety. However as films of oxide exert very great influences upon the rate of sputtering and as the cubic variety may have been coated by more oxide than the hexagonal sample these results should be considered as preliminary only.

SPUTTERED SELENIUM.

Longden,[1] Pfund[2] and Nicholson[3] have found that metallic cathodes of gray selenium when sputtered give films of amorphous material. On continued sputtering these films become black and granular.

In the present experiments a cathode of the metallic variety when sputtered at a very low current density over a period of several hours gave a film of the same character as the cathode, namely, the gray metallic modification. When the current density was increased so that the surface of the cathode became molten the sputtered sample turned to the vitreous modification which appears red by transmitted light. The thinnest parts of the gray sputtered film did not transmit red light.

Other cathodes made of the red vitreous selenium were sputtered at several current densities and in all cases gave the red vitreous variety as the sputtered film.

Attempts made to obtain x-ray photographs of the various kinds of selenium proved futile. This may be ascribed to the fact that the characteristic fluorescent radiation predominates over the scattered beams. By suitably choosing a filter to stop the selenium characteristic radiation and prolonging the exposure by the order of ten times it may be possible to obtain suitable photographs.

OPTICAL COMPARISON OF EVAPORATED AND SPUTTERED SELENIUM.

Selenium crystals were formed by using the method of evaporation described by Brown.[4] If selenium is put in a long tube heated at one end and having a uniform temperature gradient, a great variety of crystals form along the tube. These crystals have characteristic colors and structures. In the hotter portions of the tube the crystals are

[1] Longden, Am. Jour. of Sci., 10, p. 55, 1900.

[2] Pfund, PHYS. REV., 28, p. 324, 1909.

[3] Nicholson, PHYS. REV., 3, p. 1, 1914.

[4] F. Brown, PHYS. REV., 4, p. 85, 1914; 5, p. 236, 1915.

largest in size and are of metallic luster, their colors being blue-black, gray and white. At the cold edge, the amorphous red variety collects. On continued heating the red kind is transformed into the gray modification.

It is obvious that when sputtering with a high voltage and current density the temperature will be sufficiently elevated to cause rapid evaporation simultaneously with the sputtering as selenium melts at 220° C. On the other hand at low current densities the gray metallic crystals were sputtered intact, indicating that sputtering took place without appreciable evaporation of the selenium cathode. If the selenium had evaporated, the red modification would have formed, on condensing at the cold glass slide. Evidently when selenium is sputtered, under suitable conditions, no alteration of crystal structure takes place, the crystals leaving the cathode in grains.

General Discussion of Data.

Reinders and Hamburger[1] examined with the ultramicroscope films of sputtered silver and tungsten. The grains making up the silver films were found to range from 6 μ to 8 μ in diameter while those making up the films of tungsten varied from 2 μ to 5 μ. These comparatively large grains were found to be imbedded in a thin layer of amorphous metal. When sputtered at high temperatures the particles were of larger size than when sputtered at low temperatures.

In the present work it has been shown that the sputtered films are crystalline and that the crystalline particles making up the film are arranged at random orientations with respect to each other.

The writer's data show that evaporated metallic films do not consist of the pure metal in the crystalline state but of metallic compounds and amorphous metal.

It has been shown by Langmuir[2] that metallic evaporation in a fairly high vacuum takes place atom by atom. (However it appears from the work of Reinders, Hamburger, Kaye and Ewen[3] that the low melting-point elements occasionally eject large particles during the process of sublimation.) The vapor of tungsten was found to be monatomic as long as the gas pressure in the tube was kept below a definite value. At every collision between a nitrogen molecule and a tungsten atom the compound WN_2 was formed. Other gases were found to behave in a similar manner with respect to tungsten.

[1] W. Reinders and L. Hamburger, K. Akad. Amsterdam Proc., 19, p. 958, 1917.

[2] I. Langmuir, Jour. Am. Ch. Soc., 35, p. 944, 1913; 37, p. 1139, 1915.

[3] Kaye and Ewen, Proc. Roy. Soc., 89, p. 58, 1913.

Using the ultra-microscope, Reinders and Hamburger[1] found that the high melting-point elements W, C, Mo, Pt, Ni and Fe gave evaporated films that were mainly "amorphous." The low-melting metals Au, Ag, Cu and magnesium show a tendency toward a coarser condensation and seemed to form a connected network of ultra-microscopic particles.

The writer's spectrograms of the evaporated films show that the vapor in transit to the film has combined with the gases present in the tube and that if pure metal is present it exists only in the amorphous state. Indeed the conditions are favorable during evaporation in a high vacuum for the formation of an amorphous metal.

Maurain[2] has shown from magnetic deflection tests that the cathodic particles while charged electrically have the ratio e/m of such a value as to indicate that the particles in transit consist of large groups of atoms.

Lack of fluorescence when these particles impinge upon a suitable material is a further indication that the sputtered particles are large and slow moving.

In the present tests the relatively pure condition of the sputtered films indicates that the number of collisions per atom with gas molecules in transit has been small, showing that the particles in transit consist of a large number of atoms.

Concerning the origin of the sputtered particles there has been much difference of opinion in the past. Some have maintained that sputtering is an evaporation phenomenon and others have held that the particles were bodily knocked off from the cathode by the impinging gas ion. The evidence here presented seems to prove that the particles initially leave the cathode in granular crystals rather than by mon-atomic evaporation. In the latter case it would have to be assumed that the large particles in transit had been formed by condensation of the vapor near the surface of the cathode. This appears very improbable as the gas pressure used in sputtering is lower than that for which condensation of metallic vapor occurs.

Worthing and Baker[3] have recently shown that the rate of metallic evaporation is not affected by electrostatic fields of less than 800,000 volts per cm. Hence the comparatively low field strengths used in sputtering would exert no influence on the rate of evaporation or size of particles. This eliminates the hypothesis of large particles being thrown

[1] W. Reinders and L. Hamburger, K. Akad. Amsterdam, Proc., 19, p. 958, 1917; 20, p. 1135, 1918.

[2] C. Maurain, Compt. Rend., 161, p. 1223, 1905; 162, p. 870, 1906.

[3] A. Worthing and W. Baker, PHYS. REV., 17, p. 239, 1921. A. Worthing, PHYS. REV., 17, p. 418, 1921.

off by evaporation under the influence of an electric field such as that present in sputtering.

In conclusion the writer wishes to thank Mr. L. F. Curtiss for preparing many of the sputtered films and Professor Ernest Merritt for his kindly interest in the work.

CORNELL UNIVERSITY,
April, 1921.

NOTE ADDED AUGUST 16, 1921.

After this paper had gone to press articles appeared on the structure of bismuth by Ogg, Phil. Mag., 42, p. 163, 1921, and James, Phil. Mag., 42, p. 233, 1921. They report a more detailed study of bismuth using a large crystal and the original Bragg method, which of course would be impossible with thin films. The dimensions given by Ogg and James agree with those here given when expressed in the same terminology. Instead of the simple rhombohedral lattice as I have stated the structure of bismuth to be they have found it to be best represented by a slightly distorted rhombohedral lattice resolvable into two face centered interpenetrating rhombohedral lattices.

ON THE EMISSION AND ABSORPTION WAVE-LENGTHS OF THE CHARACTERISTIC RADIATION IN THE L-SERIES.

BY D. COSTER.

SYNOPSIS.

Wave-lengths of the lines L_{β_5}, L_{γ_2} and L_{γ_4} of the X-ray spectra of W, Pt, Au, Tl, Pb, Bi, Th and Ur have been measured by an improved photographic method developed by Siegbahn, for comparison with the corresponding absorption lines L_{a_1}, L_{a_2} and L_{a_3} measured by Duane and Patterson.

Test of Stokes' law as applied to X-radiation.—The conclusion of Duane and Patterson that contrary to Stokes' law the absorption wave-lengths are in some cases longer than the corresponding critical emission wave-lengths is found not to be true for any of the elements from Pt to Ur. In the case of W there is a discrepancy, but this may be attributed to the effect of the characteristic radiation from the W target used.

IN two very interesting papers Duane and Patterson[1] give the results of their measurements of the three critical absorption wave-lengths of the elements tungsten-uranium. From their measurements they conclude that these critical wave-lengths are not always shorter than the emission wave-lengths, which belong to the same part of the series, and that consequently Stokes' law breaks down in the x-ray series. Now this conclusion seems to be contradictory to many views in modern physics and especially to Bohr's theory. It therefore seems to me very desirable to examine thoroughly the experimental evidence, before drawing conclusions from these experiments.

In Prof. M. Siegbahn's laboratory, I have determined[2] the wave-lengths of most of the L-lines of the elements tungsten-uranium (the wave-lengths for tungsten have been determined by Prof. Siegbahn himself) by the photographic method, which has recently been improved in its essentials by Prof. Siegbahn.[3] As is known, the lines of the L-series are divided into three groups, which are related respectively to the three absorption bands, denoted by Duane as La_1, La_2 and La_3. The shortest lines belonging respectively to these three groups are β_5, γ_2 and γ_4. Unfortunately these lines are rather faint and they could not be measured

[1] Proc. Nat. Ac. Sci. Washington, Sept., 1920.

[2] Zeitschrift für Physik, 4, p. 178, 1921.

[3] Phil. Mag., vol. 37, p. 601, 1919.

with the same accuracy as the stronger lines α_1, α_2, β_1, β_2 and γ_1. The accuracy is sufficient, however, to allow of some provisional conclusions. In the following table I have combined the values obtained by Duane

	Wave-lengths in 10^{-11} cm.					
El.	La_1	$L\beta_5$	La_2	$L\gamma_2$	La_3	$L\gamma_4$
W	1213.6±0.1	1203.1	1072.6±0.5	1065.84	1024 ±3	1026.47
Pt	1070.5±0.3	1070.1±0.4	932.1±0.3	931.7±0.4	888.5±0.9	895.0±0.4
Au	1038.3±0.3	1038.2±0.4	899.3±0.3	901.2±0.4	860.6±0.8	866.3±0.4
Tl	977.6±0.3	978.3±0.4	841.5±0.3		805.5±1.4	810.0±0.4
Pb	949.7±0.3	949.5±0.2	813.3±0.3	813.7±0.2	780.3±0.9	783.6±0.4
Bi	921.6±0.3	922.3±0.4	787.2±0.3	787.4±0.4	753.2±0.9	761. ±2
Th	759.6±0.3	762.6±0.2	628.6±0.3	630.1±0.4	604.4±0.7	
Ur	721.4±0.3	724.1±0.4	591.8±0.3	592.6±0.4	568.5±0.7	

and Patterson for La_1, La_2 and La_3 and my values for β_5, γ_2 and γ_4, in so far as the same elements were measured.

From this table it appears that, for the elements Pt, Au, Tl, Pb and Bi: La_1 and $L\beta_5$ and also La_2 and $L\gamma_2$ coincide within the limit of possible error. For the elements Th and Ur the La_1 and La_2 wave-lengths seem to be slightly shorter then $L\beta_5$ and $L\gamma_2$. In the case of La_3, the wave-length is considerably shorter than $L\gamma_4$ for all the elements. There is consequently perfect agreement with Stokes' law.

This close agreement strongly supports our confidence, both in the ionization-method, which has been greatly improved by Prof. Duane and in the photographic method used in the laboratory of Prof. Siegbahn.

For the element tungsten however there is a remarkable discrepancy, which lies wholly outside the limit of possible error. Now it seems to me, that in the measurements of the tungsten absorption-bands there is a complicating feature which is not found in the measurements of the other elements. The bands were measured with a Coolidge-tube with a tungsten anti-cathode and a tungsten hot-wire, which gives not only a heterogeneous radiation, but also a very strong characteristic L-radiation of tungsten. Now it is known, that the heterogeneous radiation of an anticathode in the region of its own characteristic radiation is of considerably less intensity for both the long-wave and the short-wave end of the spectrum than it would be, if under the same conditions another anticathode-material were used. To determine the L-bands of tungsten in a manner quite free from criticism, it would perhaps be better to

make use of an anticathode-material other than tungsten. Moreover the tungsten hot-wire should be avoided, as by the tungsten sputtering, the anticathode would be coated with a thin sheet of tungsten. It therefore seems desirable to employ a tube of the old type for the measurements in question.

LUND, April, 1921.
PHYSICAL LABORATORY OF THE UNIVERSITY.

PHYSICAL PROPERTIES OF THIN METALLIC FILMS.[1]

III. Some Factors Affecting the Resistance of Sputtered Platinum Films.

By Lewis R. Koller.

Synopsis.

Resistance of sputtered platinum films; aging in vacuo and in various gases.—The rapid decrease of resistance which occurs if a film is kept in vacuo after sputtering, is doubtless due to coalescence or agglomeration of the particles making up the film. In air, oxygen and hydrogen, however, this aging practically stops, probably because the adsorption of gas around the particles prevents further coalescence until the gas is removed by reëvacuation or by chemical means. This adsorption theory was tested in various ways and was found in accord with all the facts. Nitrogen and carbon dioxide are only slightly adsorbed. The *effect of heating* is to accelerate and further the aging process but with prolonged heating the resistance reaches a minimum and then increases indefinitely. *Temperature coefficients of resistance* to 200° C. were measured for films previously aged at a higher temperature and were found to depend, like the resistance itself, more on the physical condition, as determined by heat treatment, than on the thickness of the film. The highest coefficient measured was 0.002 which is about 4/7 of that of platinum in bulk. Very thin films have negative coefficients.

Activation of platinum by sputtering.—Both the sputtered film and the cathode used in sputtering cause hydrogen and oxygen to combine at room temperature so rapidly that the film and the cathode may become very hot.

Historical Summary.

ONE of the most noticeable properties of thin metal films, deposited by cathode sputtering, is that they undergo a change in resistance with time. For some metals this change is an increase, for others it is a decrease, while some pass through a minimum. In general the change is accelerated by heat. This process of change in resistance with time has been called aging.

These facts have been observed by several investigators. Kohlschutter and Noll[2] found that silver films at first decrease in resistance with time after sputtering and then increase, the manner of this change depending on the nature of the film as determined by the gas in which it was sputtered and on the heat treatment which it received after sputtering. Patterson[3] found that bismuth films increase in resistance after

[1] The writer is pleased to acknowledge assistance from a grant from the Rumford Fund to Prof. F. K. Richtmyer.

[2] Kohlschutter and Noll, Zeit. fur Elektrochemie, 18, 419, 1912.

[3] Patterson, Phil. Mag., Series 6, 4, 652, 1902.

sputtering, and that platinum films decrease in resistance on heating. Longden's[1] results were similar to those of Patterson. Miss Hobbs,[2] also working with platinum, found that the films decreased in resistance when allowed to age in vacuo, but rose in resistance when air was admitted to the sputtering jar.

It was the purpose of this investigation to study the aging of sputtered films, particularly with reference to the effect on aging of adsorbed gases. Unless otherwise specified the films studied were of platinum.

DESCRIPTION OF APPARATUS AND PROCEDURE.

The sputtering apparatus was of the type usually used for this purpose and needs no special description. The high vacua when required were obtained with a Langmuir pump. Pressures were measured by means of a McLeod gauge placed on the high vacuum side of the Langmuir pump. No attempt was made to keep mercury vapor out of the sputtering jars. These were small bell jars provided with leads sealed through the glass, so that the resistance of the films could be measured in situ. Resistances were measured on a Wheatstone Bridge.

The films were sputtered on small strips of glass prepared in a manner similar to that described by Richtmyer and Curtiss,[3] and were about 11 mm. long by 13 mm. wide. The films were deposited at a pressure in the neighborhood of 0.03 mm. of mercury. In order to have fairly constant pressure conditions during deposition a discharge was first passed through the jar for about an hour. During this time the blank was protected by an aluminum shield of the shape shown in Fig. 1, which was mounted on a pivot in a horizontal position. This shield carried several small pieces of iron on its upper surface so that, when the jar was sufficiently freed of occluded gases, it could be swung around from without, by means of a magnet, and the opening placed over the blank. The distance between the blank and the cathode was from 1.5 to 3 cm. The length of the cathode dark space under the conditions of operation was about 1 cm. The necessary voltage was obtained from a transformer operating on the 110 volt circuit and was in the neighborhood of 10,000 volts. In order to avoid excessive heating of the jar and of the film during deposition, an interrupter was placed in the primary of the transformer circuit which opened the circuit for about 5 seconds out of every 6. The stopcocks in the system were

Fig. 1.

[1] Longden, PHYS. REV., 11, 40, 1900.

[2] Hobbs, Phil. Mag., 32, 141, 1916.

[3] PHYS. REV., 15, 465, 1920.

greased with a special grease having a low vapor pressure, prepared as described by Booth.[1]

Normal Aging in Vacuo.

If a sputtered film is allowed to age in the air of the laboratory its resistance will decrease rather slowly, and perhaps somewhat irregularly, for a period of many weeks or even months before it settles to a nearly constant value. If the film is allowed to age in vacuo (that is if the

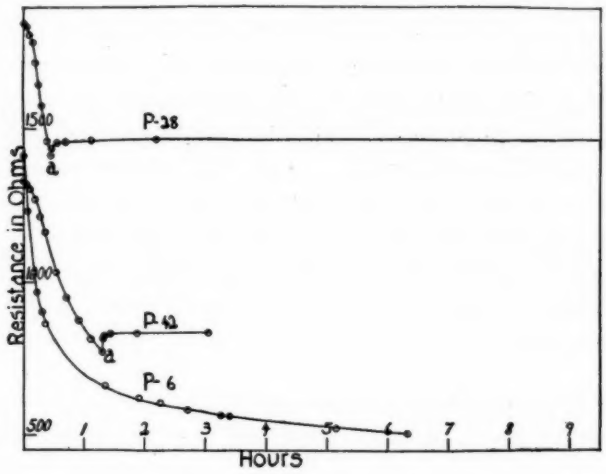

Fig. 2.

pressure is kept below 0.005 mm. by running the pumps) the time resistance curve will be of the form shown by P. 6 Fig. (2). The initial reading here was taken immediately after stopping sputtering, and the pumps were kept running during the entire course of the observations. The initial value of the resistance was about 1,400 ohms and it dropped to a final value of approximately one third of this. This curve is typical in general form for both thicker and thinner films. In all cases the resistance decreases very rapidly at first and then gradually more and more slowly until finally after about 12 hours the rate of decrease is almost negligible. In the case of thinner films the total drop is relatively greater and of thicker ones relatively less for reasons which will be discussed later. The general form of the curve, however, is the same for all films.

Evidently what is taking place here is a process of settling down and of agglomeration, or coalescence or sintering, the last three terms being more or less synonymous. In view of the lack of exact knowledge of the

[1] H. S. Booth, Thesis, Cornell University, 1919.

process coalescence is probably the best term to apply. This process has been studied for many substances both crystalline and amorphous. Bancroft[1] cites the cases of the sintering of tungsten and tantalum powders at temperatures far below the melting point and comes to the general conclusion that "liquid drops or solid grains will coalesce or agglomerate if brought into actual contact." Since we know from the work of Mr. Kahler[2] done in this laboratory that sputtered films are made up of small crystals, it is easy to form a picture of the mechanism by which the resistance is changed. The resistance of a film having this granular structure must consist of two parts; first, a purely metallic resistance, and secondly, a part due to the contacts between the particles. The first part of the resistance is not changed by aging, but the second, namely that due to the contacts, must be diminished, since as the small particles coalesce to form larger ones some of the contacts must disappear. This process, of course, can only result in a lowering of resistance when the film contains sufficient metal so that the coalescence may proceed without actually causing breaks. For this coalescence to take place readily the particles must actually come *into contact*, which can only take place in vacuo.

EFFECT OF ADSORPTION OF AIR.

If, instead of allowing the process to run to an end in vacuo, air is admitted to the jar a different result is obtained, as is shown by curves P. 28 and P. 42 in Fig. 2, where air at atmospheric pressure was admitted at the points marked *a*. The result is the same whether air is admitted immediately after sputtering or several hours later. Upon the admission of the air two things take place; first, a slight rise in the resistance of the film, and second, a nearly complete stoppage of the aging. This is due to the fact that each particle becomes surrounded with an adsorbed air film which tends to prevent further contact and coalescence. This prevention of coalescence by an adsorbed air film is merely an illustration of what takes place in every colloidal suspension; namely, the suspended material is kept from precipitating out by an adsorbed film either of a peptizing agent added for this purpose, or by an adsorbed film of the dispersion medium. In this case the disperse phase (platinum) is peptized by an adsorbed film of the dispersion medium (air). The rise in resistance is evidently due to a rearrangement of the little particles, most likely with a widening of the gaps between them as the air film is adsorbed.

[1] Bancroft, Applied Colloid Chemistry, p. 153.

[2] Kahler, PHYS. REV., 17, 230, 1921.

If this theory is correct, since true adsorption is a reversible phenomenon, it ought to be possible to remove the air film by reëvacuating the sputtering jar and then the aging ought to continue. This is shown by curve P. 22 of Fig. 3. Air admitted at the point marked *a* had brought

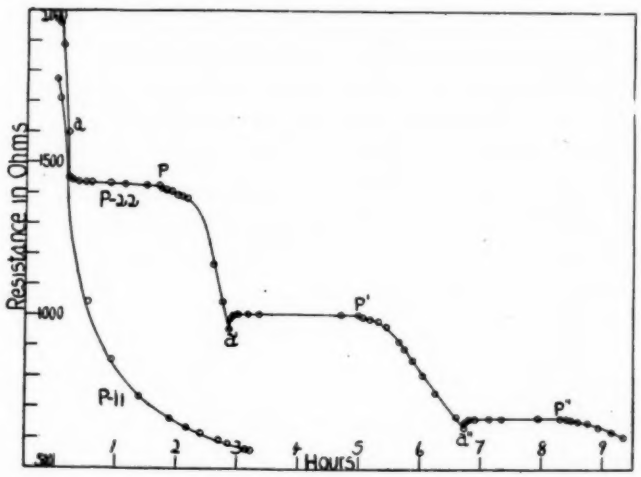

Fig. 3.

the aging to a stop. The pumps were started operating at the point marked *p*. The resistance began to fall, at first gradually and then more rapidly, until it finally reached almost the same rate of fall as before the admission of the air. At *a'* the air was again admitted and the aging stopped, and at *p'* the pumps were started with the same results as before. Similarly at *a''* and *p''*. Curve P. 11 in the figure is plotted for comparison and shows the aging in vacuo of a film having about the same initial resistance. It will be noticed that the final values of the resistance reached are of the same order, and that the corresponding portions of the aging curves are of very much the same form. The only effect of the air has been to halt the aging temporarily without producing any permanent change in the film.

A closer study of some of the portions of the aging curves gives additional evidence of the correctness of this adsorption theory. First of all consider the rise in resistance when air is admitted to the sputtering jar. The greater part of this rise takes place in the first two or three minutes and after that it continues at a gradually decreasing rate for several hours. (This behavior is characteristic of all adsorption phenomena, where the equilibrium is nearly reached in the first few minutes, but is not complete until after a lapse of several hours.) Later a slight gradual fall in resistance may take place. Although the film may continue to

age thus at a slow rate for a long time it shows no signs (over a period of several months) of dropping to the value which it would have reached if it had been aged in vacuo. The time required to reach the maximum depends on the resultant of the rate of aging and the rate of rise due to the gas.

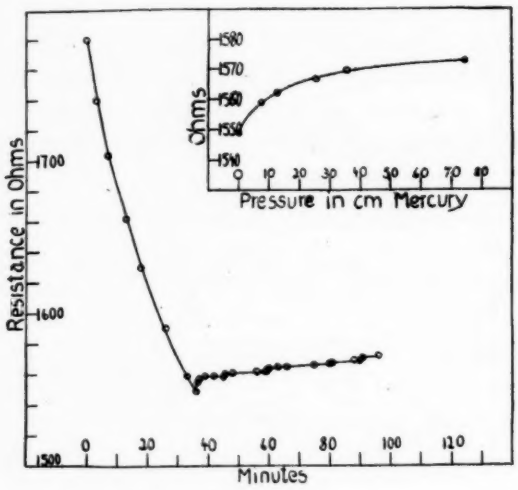

Fig. 4.

If this rise is due to adsorption of gas by the film it should be a function of pressure. This was actually found to be the case as shown in Fig. 4. In this case instead of admitting air at atmospheric pressure at once it was admitted in several instalments, allowing time in each case for equilibrium to be established. According to the theory of adsorption, at each pressure a definite amount of gas must be adsorbed, corresponding to which there is a definite value of the resistance of the film. A further increase in pressure will result in more gas being adsorbed and a further rise in resistance. When the final values of resistance are plotted against pressure a smooth curve is obtained, similar in general form to the adsorption isotherm.

On reversing the process and pumping out the air the exact same curve is not reproduced. The resistance drops slowly with decreasing pressure until in the neighborhood of 0.020 mm., below which it falls off very rapidly. Apparently once the aging has been stopped only a very small amount of adsorbed gas is required to prevent it from continuing, whereas it takes a much larger amount of gas to bring it actually to a stop. This is shown by a closer study of the portions of the curve marked p in Fig. 3. This has been plotted to a larger scale as curve 1 in

Fig. 5. If the values of resistance are plotted against pressure instead of time the result is shown by curve 2 in the same figure. This shows the gradual decrease in resistance till in the neighborhood of 0.020 mm. and the more rapid rate of fall as the pressure falls below this. This also explains the apparent lag observed at the beginning of many of the aging curves. This is not really a time lag of the films, but merely represents the time required for the pumps to bring the pressure from the sputtering value down below the critical value.

The pressure at which the films are sputtered is well above the critical value. This was shown by closing the stopcock leading to the sputtering jar immediately after sputtering, thus keeping the film at the pressure at which it was sputtered. When this is done the aging is very slight and the resistance time curve is nearly flat. As soon, however, as the stopcock is opened and the pumps are started the adsorbed air is given off and the resistance drops very rapidly.

Effect of Adsorption of Gases other than Air.

Some rough qualitative experiments were undertaken to determine the behavior of the films towards gases other than air. Since adsorption is a specific phenomenon the behavior of the films ought to vary with the nature of the gas, which was found to be the case.

One factor which influences the resistance of the films greatly is that the process of sputtering activates the platinum so that both the sputtered film and the cathode from which it was sputtered cause hydrogen and oxygen to combine at room temperature. This reaction takes place very rapidly; both the cathode and the thick deposits on the walls of the jar becoming quite hot, while water vapor is condensed on the cooler parts of the jar. The platinum deposits on the edges of the mica backing of the cathode are heated to incandescence and cause a mixture of hydrogen and oxygen to explode. This property of platinum is well known but so far as the writer is aware this method of activating platinum by sputtering is new. In this connection it would be interesting to study the catalytic properties of other sputtered metals; and also to see whether the substances which are known to poison catalysts have any effect on sputtering, and whether substances which are known to prevent sputtering have any effect on catalysts.

Instead of admitting air to the sputtering jar, as already described, its chief constituents were tried separately. Nitrogen in small quantities (pressure 2–3 cm.) hardly affects the aging appreciably. At a pressure of one atmosphere it slows the aging down very much but does not bring it absolutely to a standstill. Even a small amount of oxygen

is effective in stopping the aging and giving the characteristic rise which has already been described; while increasing the concentration (pressure) of the oxygen gives further rises in resistance. This shows that the active constituent of the air is the oxygen, which is strongly adsorbed, while the nitrogen is only taken up to a much lesser extent.

Carbon dioxide behaves in much the same manner as nitrogen.

If hydrogen is admitted, after oxygen has been admitted and pumped out again, the resistance of the film will drop several hundred ohms almost instantaneously, and will continue to fall at a gradually decreasing rate for some time. This is due to two causes. One is the heat developed by the reaction of the hydrogen with the oxygen previously adsorbed by the film, which accelerates the aging; and the other is due to the removal of the oxygen from the surface of the particles by combination with the hydrogen, which has the same effect as pumping. An increase in the hydrogen pressure will result in a further drop in resistance because the velocity of the reaction between the hydrogen and oxygen is a function of the pressure. Hydrogen has the same effect even if oxygen has not been previously admitted because the film contains oxygen which was adsorbed during the process of sputtering. When the hydrogen oxygen reaction has run to an end the aging is gradually brought nearly to a stop by the adsorption of hydrogen.

If the hydrogen is nearly completely removed by pumping and oxygen is admitted the characteristic rise is observed. This is because the oxygen is much more strongly adsorbed than the hydrogen, and the rise due to the adsorption of oxygen masks the heating effect of the reaction with the very slight amount of hydrogen in the film. If now the oxygen is removed by pumping and hydrogen is readmitted another sudden drop will take place due to the heating when the hydrogen combines with the additional oxygen which has been taken up by the film. Miss Hobbs[1] observed that when a film has been deposited in hydrogen the effect of admitting hydrogen is a rise in resistance, while in the case of a film which has been deposited in air the hydrogen may produce a fall in resistance which seems to substantiate the writer's theory.

Illuminating gas has the same effect as hydrogen (to a slightly lesser extent) probably because it contains a large percentage of hydrogen.

It was found that at times the admission of air caused a sudden drop in resistance instead of the usual rise. This effect is shown at *a* in Fig. 3. This is due to the presence of traces of illuminating gas in the air of the laboratory.

[1] *Loc. cit.*

Temperature Coefficients.

Another very interesting property of sputtered films is that their temperature coefficients of resistance are smaller than the temperature coefficients of the same metal in bulk. Patterson[1] made some measurements of the temperature coefficients of platinum films and found an apparent relation between the temperature coefficient and the thickness. Swann[2] also made measurements of temperature coefficients on the basis of which he formulated a theory of the mechanism of conduction in thin films. According to Swann's theory the films owe their properties to their granular structure and not to their thickness. Longden[3] measured the temperature coefficients of very thin films and found them negative. Thicker films had positive coefficients, and some intermediate films had zero coefficients. Longden attempted to show from

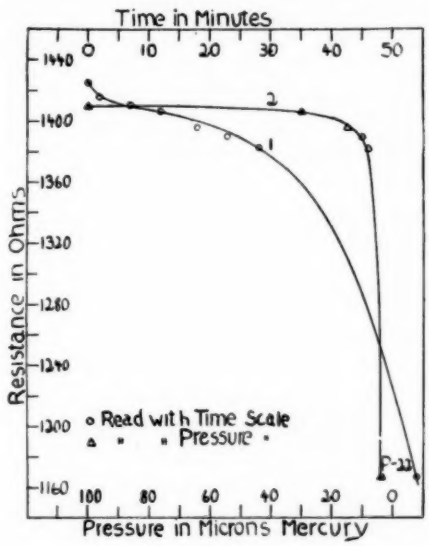

Fig. 5.

his work that there was a linear relation between thickness and temperature coefficient.

In this part of the work the resistances were measured as before on a Wheatstone Bridge. The films were in a test tube placed in an oil bath, which was electrically heated and constantly stirred. Temperatures were read on a thermometer immersed in the oil. The measurements covered the range from room temperature to 200° C.

The first time a film is heated its resistance may show an initial rise

[1] *Loc. cit.*

[2] Swann, Phil. Mag., 28, 467, 1914.

[3] *Loc. cit.*

or it may begin to fall at once, but in all cases on further heating the resistance falls quite rapidly. This initial difference in behavior is probably due to the fact that the films were of different ages and had reached different stages in the aging process. The rapid drop in resistance when plotted against temperature gives a smooth curve which is rather misleading. This change in resistance is really a time effect and since the temperature of the bath is also a function of the time the resistance and temperature seem to be related. While the film is being heated two changes in resistance are taking place simultaneously. One is a small rise due to the temperature coefficient. The other is a large decrease due to the more rapid aging at the higher temperature. The higher the temperature is raised above room temperature the greater does the latter become, and until it has proceeded nearly to an end it completely masks the temperature coefficient effect. Thus with each heating the resistance of the film is permanently lowered. After several

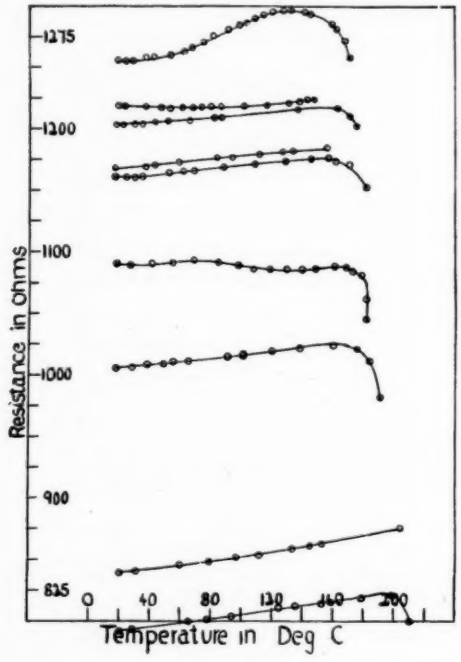

Fig. 6.

such heatings, when the resistance has nearly reached its minimum value the temperature coefficient becomes perceptible, and the heating and cooling curves become nearly straight lines and can be duplicated, provided the temperature is kept well below the maximum temperature of the previous run. Such a series of curves is shown in Fig. 6.

As the initial resistance of the film becomes lower with each run the temperature coefficient becomes greater but the slope of the lines changes very little. This agrees well with the suggestion made before as to the mechanism of aging; the effect of heating is to increase the resistance of the metallic portion of the film due to the true temperature coefficient effect, and to decrease the resistance of the contacts due to eliminating many of them as the particles coalesce. Until the film is well aged the latter effect is by far the greater. As long as the temperature of a film is kept below a higher temperature to which it has previously been raised the aging is small and so the chief change is in the true metallic resistance, and this rise must remain nearly the same for all stages of the aging.

The temperature coefficient then becomes a function of the degree of aging which in turn depends on the temperature to which a film has been heated. If, for example, a film is placed in the oil bath at a temperature of 100° the resistance will fall rapidly at first but after some hours will settle to a nearly constant value. The film will now be quite permanent for all temperatures below 100° and the temperature resistance curve will be nearly a straight line, as long as the temperature is kept below this value. On heating to say 200° aging proceeds further with a still further lowering in the resistance of the film until it finally reaches a constant value again. Again after this treatment the temperature resistance curve will be a straight line, while the temperature coefficient will have been nearly doubled. Patterson assumed that his films were

TABLE I.

Film No.	Initial Resistance.	Temperature Coefficient.	Patterson's Temp. Coef.
85	1570	.000888	.00011 to .00033 approx.
77	1444	.000644	
72	1974	.00108	
58	1866	.00075	
73	506	.00108	
70	93	.00144	.0005 approx.
55	65	.00200	

completely aged by heating them for 60 hours at 100°, but the present work shows that heating to still higher temperature would have reduced the resistance still more and multiplied his temperature coefficients by as much as 4. After aging at the highest obtainable temperature of the oil bath (210°) the films were heated in an oven of which the temperature was estimated to be 500° C. This resulted in a still further lowering

of the resistance and raising of the temperature coefficient. In some cases the resistance became infinite due to the destruction of the gold platinum contact. In such cases a new pair of gold terminals was sputtered overlapping the old ones. This merely changed the effective length of the film. Table I. gives the initial resistances and the maximum values of the temperature coefficients obtained for some of the films, and for comparison the values for films of the same thickness obtained by Patterson. Very thin films were found to have negative temperature coefficients.

The aging due to heating even if done in air is very much greater than that due to a vacuum. The effect of heat is to accelerate the rate of aging, and furthermore heat will reduce the resistance far below the minimum value reached in vacuo at room temperature. For example, a film which had dropped to 376 ohms when aged in vacuo was heated for several hours at 110° and finally reached a value of 316 ohms. On further heating at 200° the resistance dropped to 192 ohms.

On prolonged heating at the higher temperatures the resistance of all except the very thickest films passes through a minimum, becoming very large and finally infinite. This point of minimum resistance is reached at lower temperatures the thinner the films. The explanation given by Kohlschütter and Noll for a similar phenomenon in the case of silver films probably holds good here, namely that as the coalescence proceeds it finally reaches a point where there is not sufficient metal in the film for it to take place without rupturing the film. In this condition the films must be very much like the extremely thin films in which Swann describes the distribution of particles as being similar to the condition of affairs on a pavement when rain drops begin to fall, and before enough drops have fallen to cover the pavement. The difference probably is that in the case of films which have been brought to this state by excessive heat treatment the individual particles must be larger. Since the very thin films have negative temperature coefficients it would be expected that these high resistance thick films would also have negative coefficients. These films, however, are in such an unstable condition that it is extremely difficult to make measurements with any degree of certainty. One such film was found to have a negative coefficient, but although several other films were studied this could not be confirmed.

A study of Table I. will show that the thickest films have the largest temperature coefficients and that the values decrease as the films become thinner. The maximum value is about four sevenths of the value of that for platinum in bulk. These values are higher than the ones obtained by Patterson because the aging was carried on at higher temperatures and therefore proceeded further. The fact that the tempera-

ture coefficients increase with increasing thickness is probably not due to the thickness or thinness of the film, but to the fact that the thinner films could not be aged to the same point as the thicker ones without destroying them. In other words the temperature coefficient of a film depends not on its thickness but upon its degree of agglomeration. Probably all films have the same temperature coefficients when aged to the same point.

Films deposited on quartz were found to have the same temperature coefficients as similarly treated films of the same thickness on glass.

In the table the initial resistances of the films are given, but as a matter of fact a serious error would be introduced if the thickness of films was to be determined on the basis of a comparison of initial resistances. A film having a resistance of the order of 10^6 ohms will fall on heating to 10^3 ohms, while one having an initial resistance of 1,000 ohms will fall under the same conditions to 100 ohms. The ratio of the final conductances of these two films, which is about the same as the ratio of the times of sputtering, gives a true idea of the amount of metal in them; while the ratio of the initial conductances would be entirely misleading. The reason for this is that the films age during the process of sputtering, probably partly due to the impact of the particles and mainly due to the heating. Thus a thicker film, which during the course of sputtering has been exposed to more heating has therefore aged more and so for the same amount of metal has a lower resistance.

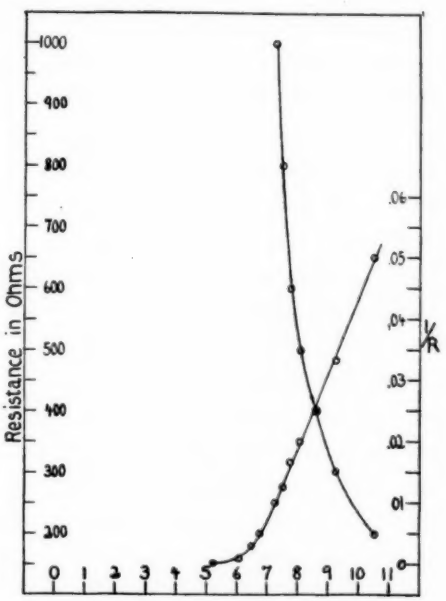

Fig. 7.

The aging due to the heat of sputtering was tested as follows. A film was sputtered in the usual way and the aging stopped by admitting air. A thin microscope cover glass was then placed directly on top of the film and the jar reëvacuated. At a pressure well above that at which aging takes place a film was sputtered on this cover glass. This resulted in a rapid drop in resistance which can only be explained by the heating effect of the sputtering.

In order to obtain some more information in regard to what takes place during sputtering measurements of resistance were made while sputtering and plotted against time as shown in Fig. 7. The reciprocals of these resistances when plotted against time give a straight line excepting during the very early stages of the deposition. If the conductivity increased by equal increments in equal times this curve should pass through the origin. The fact that it does not do so indicates that during sputtering in addition to depositing more metal the resistance of the metal already deposited is also growing less, thus giving the line a steeper slope than would be due to deposition of metal alone.

According to the theory of J. J. Thomson there should be a rapid increase in resistance below a certain critical thickness; this critical point being that at which the dimensions of the film become comparable with the mean free path of an electron. Patterson's results seem to show that the specific resistance of the films increases very rapidly with decreasing thickness below a thickness of 7×10^{-7} cm. which is in accordance with the theory. From this bend in the specific resistance thickness curve Patterson computes the mean free path of an electron. It is extremely doubtful whether the Thomson theory can be applied directly to sputtered films, the thickness of which is an indefinite quantity. In some places where the groups of crystals are piled up the thickness may be comparatively great while in others it may be very much less. While the specific resistance undoubtedly depends on the thickness the conditions in the film are such that the thickness is not uniform, and the Thomson theory which has been developed for uniform films does not necessarily apply here. The *physical condition* of the film is probably a much more important factor than the thickness.

Patterson's films were all aged at a temperature of 110°. Heating to a higher temperature would have lowered the resistance of all of them, but very likely not in the same ratio, and the thicker ones would probably have been lowered more than the thinner ones, so that possibly the shape of Patterson's specific resistance thickness curve would be altered.

Swann treats the films as "groups of molecules not pressed into intimate contact so that it is only those electrons which have more than a certain minimum velocity, depending on the closeness of packing, which

can travel from one group to the next. This necessary velocity gets less as the time of deposit increases and the groups are pressed more intimately into contact by the greater molecular forces brought into play." This theory seems in accordance with the facts observed in the present work. The numerical values of Swann, however, are open to the same criticism as those of Patterson, namely that the films were insufficiently aged.

In conclusion the writer wishes to express his thanks to Professor Richtmyer who suggested the problem and whose enthusiasm and encouragement made the work possible.

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THE DISTINCTION BETWEEN INTRINSIC AND SPURIOUS CONTACT E.M.F.S AND THE QUESTION OF THE ABSORPTION OF RADIATION BY METALS IN QUANTA.

BY R. A. MILLIKAN.

SYNOPSIS.

Stopping potentials for photo-electrons from Na, K and Li surfaces, as determined with a Faraday cylinder in vacuo for monochromatic ultraviolet light, were found to be accurately the same for all. This result makes general the conclusion that the stopping potential for a given frequency is the same for all clean metals. It is not the same for an *oxidized copper surface*, however, or for any surface showing a spurious contact e.m.f.

Contact e.m.f.'s between Na, K and Li and the oxidized Cu surface of a Faraday cylinder were not found to be constant, but their changes were found to keep pace exactly with changes in the common stopping potential. These changes are attributed to the entanglement of electrons in the copper oxide surface, thus giving rise to a spurious e.m.f.

Intrinsic contact e.m.f. between any two metals is shown to be a definite quantity equal to $(h\nu_0 - h\nu_0')/e$, when ν_0 and ν_0' are the threshold frequencies for photo-electric emission from the two metals. This equation enables intrinsic to be *distinguished from spurious contact e.m.f.* For if the observed contact e.m.f. differs from this value, (which it does not do for clean metals), there is a spurious contact e.m.f. equal to this difference and also equal to the difference in stopping potentials.

The Photo-electric quantity $h\nu_0$ is shown to be equal to the thermionic work function ϕe measured at the same temperature.

Theory of photo-electric emission.—Proof is adduced for the conclusion that either the free, conduction electrons of a metal have the power of taking up the energy $h\nu$ from the incident light, or that, as Barkla has claimed, absorption does not take place in whole quanta. The difficulties associated with each conclusion are pointed out.

I. INTRODUCTION.

THE present paper is a continuation of, and a supplement to, one published in 1916, under the title "Einstein's Photoelectric Equation and Contact Electromotive-Force,"[1] in which there were pointed out certain necessary conclusions of great importance for the theory of quanta which might be drawn from a given type of photoelectric observations. At that time, however, it had not been possible to make these observations in full and report upon them was therefore deferred, the immediate object there being to obtain evidence for the then unsettled question as to the validity or invalidity of an equation of the type first suggested by Einstein.

[1] PHYS. REV., VII., 18, 1916.

In view of the extraordinary sequence of exact determinations of h made with the aid of the Einstein relation, or its inverse suggested earlier by Bragg, a sequence which began with the author's studies in the region of ordinary wave-lengths,[1] and was continued by those of Duane, Hunt, Hull, and others, in the field of general x-radiation, then by those of Webster and others in the field of characteristic x-rays, and finally by those of McLennan, Foote, and a large group of observers in the field of ionizing potentials, we may now set down without fear of error the following equation as representing accurately the facts of observation, whatever may have been, or may now be, its theoretical basis:

$$\tfrac{1}{2}Mv^2 = (PD + K)e = h\nu - w = h\nu - h\nu_0 \qquad (1)$$

in which v is the velocity with which a negative electron escapes from a metallic surface under the influence of a given frequency ν; w the work which it does in getting out of the metal; ν_0 the threshold value of the frequency, or the smallest value of ν which is capable, even with a strong accelerating field (say 20 volts), of detaching a negative electron from the metal at all; PD the stopping potential, or the positive potential which must be applied to the metal to just prevent the escape from it of a photo current, under the influence of the impressed frequency ν, and K the contact e.m.f. between the illuminated metal and the Faraday cylinder into which the liberated electron must escape if it gets away at all.

The introduction of the term K represents an improvement upon Einstein's equation, the necessity for which was first seen, clearly stated, and in large part experimentally justified by Richardson and Compton,[2] and the correctness of which was very accurately demonstrated by the author, by simultaneous observations *in vacuo* under identical conditions of contact e.m.f.s, stopping potentials and threshold frequencies (*l.c.*).

Now if we *assume* as was done in the 1916 paper, and as has in general been done by all workers in the field of the emission of electrons under the influence of ether waves, *that the photo-electrons come from the atoms of the metal*, an assumption which is apparently justified by the independence of both photo-currents and stopping potentials upon temperature, as well as by the fact that insulators have been shown by the oil-drop methods to exhibit a photo-electric behavior precisely like that of conductors,[3] then the w term in (1) must be made up of two parts w_1 and w_2, the former w_1 representing the work necessary to detach the negative electron from its parent atom, and the latter w_2 representing

[1] PHYS. REV., VII., 355, 1916.

[2] Phil. Mag., 24, 592, 1912.

[3] Cf. M. I. Kelly, PHYS. REV., 16, 260.

the work necessary to push the free electron through the surface of the metal. This last term must be precisely the same as that which Richardson has denoted by the product φe in his development of the thermionic equations.

If, now, we push two metals A and B in succession before the Faraday cylinder F (see Fig. 1), set up equation (1) with respect to each of them, and subtract, as below, we may make ourselves independent of a measurement of a contact e.m.f. between either metal and the Faraday cylinder. Thus we have

$$(PD_A + K_A)e = h\nu - h\nu_{0_A} = h\nu - (w_{1_A} + w_{2_A})$$
$$(PD_B + K_B)e = h\nu - h\nu_{0_B} = h\nu - (w_{1_B} + w_{2_B})$$

which give, by subtraction

$$(PD_A - PD_B)e + (K_A - K_B)e = (w_{1_B} - w_{1_A}) + (w_{2_B} - w_{2_A}) = h\nu_{0_B} - h\nu_{0_A}. \quad (2)$$

Now, $K_A - K_B$ is the contact e.m.f.$_{AB}$ (*i.e.*, the contact e.m.f. between the metals A and B), and *by definition* $(w_{2_B} - w_{2_A})/e$ is also the contact e.m.f.$_{AB}$. It follows, then, at once from (2), as I pointed out in 1916, that

$$(PD_A - PD_B)e = w_{1_B} - w_{1_A} \quad (3)$$

and also that

$$\text{Contact e.m.f.}_{AB} = \left(\frac{h\nu_{0_B} - h\nu_{0_A}}{e}\right) - (PD_A - PD_B). \quad (4)$$

Equation (4) then, each term of which is capable of direct and independent measurement, must be found satisfied in all cases if Einstein's equation, as modified by Richardson, is correct, and it was subjected to searching experimental test in my former work and found to be always in agreement with observation. The term $h\nu_{0_A}$ for freshly cut lithium, for example, was measured by applying a potential of about 20 volts between the lithium and the Faraday cylinder (see Fig. 1), the inner surface of which was heavily oxidized so as to render it as light-absorbing as possible, and the wave-length of the incident light was then varied until the threshold frequency was found at $\nu_0 = 57.0 \times 10^{13}$ ($\lambda = 5263$ Å). In this experiment, the negative terminal of the 20-volt battery was of course connected to the lithium. The $h\nu_{0_B}$ for the copper oxide was then found by reversing the terminal of the battery and varying the wave-length of the light incident upon the lithium until this light, strongly reflected from the lithium surface to the inside of the cylinder, began to cause negative electrons to flow from the cylinder back to the lithium. ν_{0_B} was thus located at 118.2×10^{13}. ($\lambda = 2535$ Å.) This

gave $h/e\,(\nu_{0_B} - \nu_{0_A}) = 2.53$ volts. A contact e.m.f. measurement was then made in vacuo by the Kelvin method, by turning the lithium surface through 90° to the position A' (Fig. 1) in a manner which has been previously described[1] and finding directly the potential which had to be applied to just neutralize the contact e.m.f. between it and a copper disc D, oxidized in every way as had been the copper Faraday cylinder. This measured contact e.m.f. was in the foregoing case 1.52 volts. Now, using line $\lambda = 2535$, the measured stopping potential for the lithium was found to be 1.00 volts, while for the CuO, whose threshold frequency lay at line 2535, it was of course 0. Equation (4) then gave, inserting numerical values, $1.52 = 2.53 - 1.00 = 1.53$ which is an identity within the limits of experimental error.

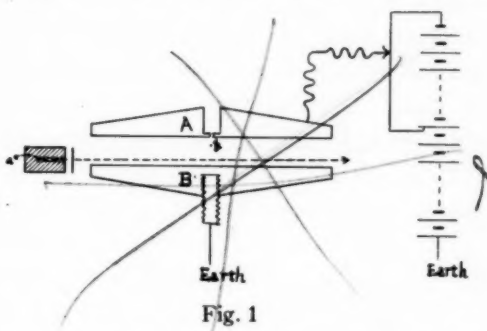

Fig. 1

I have thus given again one complete set of observations taken from the preceding work, to show how large the term $(PD_A - PD_B)$ often was, in this case a full volt, and to show how impossible it is that in these observations the contact e.m.f. can be given by the simple relation, contact e.m.f. $= h/e\,(\nu_{0_B} - \nu_{0_A})$. *I have now made many observations by the foregoing method using all three of the metals, sodium, potassium, and lithium, maintained all the time at a vacuum of* 10^{-5} *or lower and although the measured contact e.m.f.s do not in general remain at all constant over long periods of time, creeping in general towards smaller values, and showing variations in a month or two of time amounting to as much as a volt, the changes in the stopping potentials always keep pace with those in contact e.m.f. so that equation* (4) *has never yet been found to fail.* In a word, then, so far as the relations between photoelectric and contact effects are concerned, the demands of Einstein's equation are still found to be fully satisfied.

But, as pointed out in the preceding paper, there have been very strong experimental indications that a contact e.m.f. equation much more limited in scope than (4) actually holds in most cases, namely,

$$\text{Contact e.m.f.} = \frac{h}{e}\,(\nu_{0_B} - \nu_{0_A}) \qquad (5)$$

and the purpose of the present paper is to present the limits of validity of (5) and the reason for its failure in the above work, and also to discuss

[1] PHYS. REV., 7, 362, 1916.

its significance both with relation to the theory of contact e.m.f.s and the theory of quanta.

2. Intrinsic and Spurious Contact E.M.F.s.

Equation (5) was thought by Richardson and Compton[1] to be consistent with their photoelectric work, but their contact e.m.f.s were either taken from tables or, in certain instances, measured in air, so that the point in question could not be considered as in any way settled by their measurements, since $(PD_A - PD_B)$ might well be expected to be small. The most refined and convincing way of testing it should consist in bringing different metals in succession before the same Faraday cylinder, and observing whether, with a given incident frequency, the stopping potential for the different metals is the same; equations (2) and (4) show that if $(PD_A - PD_B) = 0$ contact e.m.f. must be given by $h/e\ (\nu_{0_B} - \nu_{0_A})$. This was first done by Millikan and Winchester[2] in very early photoelectric work, designed primarily to test temperature effects. We did not use monochromatic light, however, and a number of metals were essentially in the same Faraday cylinder at one and the same time, with the consequent possibility of exerting a mutual influence upon one another's fields. The observed differences in stopping potentials, in general small, are not therefore convincing. Page[3] obtained *no* differences in stopping potentials when he used freshly scraped surfaces of copper, aluminum and zinc, and Drs. Hennings[4] and Kadesch in the Ryerson Laboratory, extended Page's conclusion to a considerable number of other metals.

In the 1916 paper, I left for further study the cause of the unquestionably different result which I had obtained in working with two surfaces one of which was an alkali metal and the other the oxide of copper.

I have now to report a considerable number of further observations, made with the same apparatus, in which all of the alkali metals, Na, K and Li, were brought in succession before the Faraday cylinder with the result that *the stopping potential was always exactly and accurately the same for them all, provided the observations were made at the same time.* It made no difference whether one of the metals had recently been shaved in vacuo and the other surface similarly treated weeks earlier, or whether they had all been shaved together. In other words, no surface effects due to residual gases modified the equality of the stopping potentials. The contact e.m.f.s taken at essentially the same time, between each of

[1] Phil. Mag., 24, 592, 1912.
[2] Phil. Mag., 14, 201, 1907.
[3] Am. Jr. Sci., 36, p. 501, 1913.
[4] Phys. Rev., 8, 217, 1916.

these three metals and the oxidized copper plate differed among themselves by very appreciable amounts. However, when the apparatus was allowed to stand for some days, or for weeks, the common stopping potential would be found to have changed, in one instance by more than 1 volt, but it had shifted by the same amount for all the metals, so that the equality between the stopping potentials for the different metals remained exact. Further, the measured contact e.m.f.s were all found to have shifted by precisely the same amount as the stopping potentials. *This shows clearly that the change which had taken place was due to the element which was common to all the measurements, namely the heavily oxidized surface of copper.* Further, the direction of the change was such as to be consistent with the view that it was due to the charging of the oxide negatively by the simple retention of a swarm of negative electrons by it. The oxide coating acts like a condenser of essentially infinite capacity, but the charge on this condenser varies with the time. This charging up of the copper oxide gives rise to a "spurious contact e.m.f." which was responsible for the finite value of $(PD_A - PD_B)$ in the work discussed above. It has no effect upon $(\nu_{0_B} - \nu_{0_A})$ because in the measurement of these threshold frequencies very strong accelerating potentials are externally applied. These completely neutralize any effect of a surface charge. But in the measurement of contact e.m.f. and stopping potential, the surface charge pushes each by the same amount in the direction of negative potentials. This is why the measured contact e.m.f. between sodium and the oxidized plate was at first observed to be about 2.5 volts, but had later fallen to less than .5 volt.

The accompanying experiments, then, taken in connection with those of Page and those of Kadesch and Hennings, show in the most beautiful, quantitative way that all clean metals possess intrinsic contact e.m.f.s and they also establish a criterion by which intrinsic and spurious contact e.m.f.s may be distinguished, namely this:

If equation (5) *is found by experiment to be satisfied, only intrinsic contact e.m.f.s are present. If equation* (5) *is not found to be satisfied, then the difference between the observed contact e.m.f. and* $h/e \cdot (\nu_{0_B} - \nu_{0_A})$ *is a measure of the presence and amount of a spurious contact e.m.f.*

Thus the century-old dispute as to the reality of intrinsic contact e.m.f.s appears to be quite definitely settled by experiments of this type. The experiment of bringing sodium and platinum, for example, in succession before the same Faraday cylinder and finding the stopping photo-potentials exactly the same for the two, despite the fact that the electron leaves the sodium under the influence of a given frequency, (*e.g.*, that corresponding to $\lambda = 2535$ Å.), with a much higher velocity

than that with which it leaves the platinum, the threshold frequency for sodium being less than one half its value for platinum, is the most striking proof that each metal creates about itself a contact field which is inversely proportional to the work required to detach the electron from the metal. It is to be emphasized, too, that the result is a purely experimental one which is quite independent of any theory, although it is beautifully in accord with the theory of electron atmospheres.

3. Significance of the Foregoing Results for the Theory of Quanta.

A finite value, then, of $(PD_A - PD_B)$ is merely a measure of the surface charge on the oxide and in no case a measure of the difference in the amounts of work necessary to detach an electron from two different metallic atoms, as is implied in equation (3), since in the case of all *clean* metals or indeed in the case of metals contaminated with invisible surface films this difference is zero; *i.e.*, $(PD_A - PD_B)e = 0$ and therefore (cf. (3)) $w_{1_B} - w_{1_A} = 0$. Now, the fact that $w_{1_B} - w_{1_A} = 0$ necessitates one or the other of two alternatives:

1. Either the works necessary to detach an electron from the atom of platinum and the atom of sodium, for example, are the same, or else,

2. The photo-electron which escapes with the highest velocity from a metal under the influence of the incident frequency ν has exactly the energy $h\nu$ *when it arrives at the inner surface of the metal on its way out, no loss of energy* w_1 *in getting out of the atom having to be taken into account.*

The first of these alternatives is so violently at variance with our definite knowledge of the relative strengths of the bonds which hold the outer electrons to different atoms (cf. the values of ionizing potentials, etc.) that it may at once be dismissed as impossible. If this be admitted *we have, then, no alternative but to adopt* (2) *as the inevitable consequence of the experiments discussed in this report.*

These experiments then prove conclusively in any case that *at the same temperature there is complete identity between the photoelectric work function* $h\nu_0$ *and the thermionic work function* φe. This identity has always been assumed by Richardson, but the experimental evidence has not heretofore been exact enough to demonstrate the correctness of the assumption. No comparison of experimental values of $h\nu_0$ and φe is likely to be as trustworthy as the foregoing evidence.

The significance of (2) for the quantum theory is found in the fact that it, in turn, requires one or the other of the two following alternatives:

(*a*) Either the incident light is able to take hold of a free electron of the metal and impart to it an energy $h\nu$, or

(*b*) The incident light energy is not absorbed in whole quanta at all, but rather absorption continues within the atom until the electron is able to *escape* from the atom with the energy $h\nu$, the absorption being then $h\nu$ plus w_1, w_1 being the amount required to pull the electron out of the atom.

This last is precisely the conclusion which Barkla has drawn from his measurements upon the ionizing energy of the corpuscular radiations stimulated by characteristic x-rays.[1] I am not disposed to insist here upon the inevitableness of Barkla's conclusion, but I do wish to insist that the foregoing considerations demand either Barkla's conclusion or else the conclusion that a *free electron of a metal is able to absorb energy from an incident light wave and to be endowed by that wave with the energy* $h\nu$; *for they demand that within the metal there be free electrons which possess the full value of the energy* $h\nu$.

Either of the conclusions (*a*) or (*b*) required by these experiments is confronted by difficulties. It is very difficult to accept Barkla's conclusion (*b*) because it means either that there are an infinite number of natural frequencies within a metal, or else that an electron within an atom has the power of absorbing a quantity of energy which is characteristic of itself plus a quantity $h\nu$ which is characteristic only of the incident light. Neither of these assumptions is rationally satisfactory.

On the other hand, the conclusion that the free electrons of the metal take part in the photo-effect would seem to require that stopping potentials diminish with increasing temperature, and also that there be discontinuities in the photo-current potential curve corresponding to the potentials at which the photo-currents due to the bound electrons begin to add their effect to that of the free electrons. Neither of these predictions is as yet in harmony with the facts of observation. It is true that in the experiments of Winchester and the author[2] upon the effect of temperature upon photo-effects, the temperature was carried through but about 300° C. in the case of aluminum and about 100° C. in the case of other metals, and it is possible that a small temperature effect escaped detection. It is also conceivable that a further search for discontinuities in the photo-current potential curve might reveal them. Such a search for discontinuities and for a temperature variation in stopping potentials is now being made.

At any rate, I am at present disposed to adopt alternative (*a*) and to regard the present experimental work as justifying the conclusion that a light wave has the property of being absorbed by a *free* electron of a

[1] Phil. Trans., A, Vol. 27, 315–360, 1917.

[2] Phil. Mag., 14, 201, 1907.

metal and of imparting to that electron the energy $h\nu$. If this conclusion is correct it is of much importance for the theory of radiation, for it means that the burden of accounting for the emission of electrons with the energy $h\nu$ can no longer be thrown back upon some unknown mechanism in the structure of the atom where many physicists have in the past sought to place it.

Nor, on the other hand, can this burden be placed upon the elastic-solid properties of the complex of atoms and free (*i.e.* conduction) electrons constituting a metal. For, although, in view of the Debye and Born types of analysis of the phenomena of specific heats, etc., this complex should possess a practically infinite number of natural frequencies, each of which might get into resonance with the impressed wave of frequency ν, yet the phenomenon of discharging electrons with this energy would then be limited to systems which possess these elastic solid properties, *i.e.* to solids or at most to liquids. Gases, on the other hand, would be excluded from the possibility of exhibiting it. Yet, though exact quantitative proofs for the case of gases are perhaps not yet available, the evidence yielded by many experiments, including those of C. T. R. Wilson, upon the emission of secondary electrons from the atoms of gases by gamma and x rays is so convincing that it is at present extremely unlikely that gases do not emit electrons with energies which are at least approximately equal to $h\nu$.

If then conclusion "a" above is valid *the only remaining alternative is to consider the property of taking hold of an electron, whether free or bound and imparting to it an energy $h\nu$, as an intrinsic property of light itself.*

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X-RAY ANALYSIS OF THREE SERIES OF ALLOYS.

By Mary R. Andrews.

Synopsis.

Crystal structure of three series of alloys has been determined by Hull's method of x-ray analysis, using sheets of collodion or zapon in which the filings or powders to be investigated were embedded.

The *Fe-Ni and Fe-Co series* of pure binary alloys were each found to be solid solutions of one metal in the other with a single region of transition at 22–30 per cent. Ni and at 80–90 per cent. Co respectively. This means that Fe atoms can be substituted for up to 70 per cent. of the Ni atoms in the face-centered Ni lattice and Co atoms can be substituted for up to 80 per cent. of the Fe atoms in the cube-centered Fe lattice without changing the crystal structure. No evidence of a compound Fe_2Ni was obtained.

Fe-Ni alloys develop the cube-centered form when made magnetic by chilling in liquid air.

The *Cu-Zn series* of alloys form solid solutions of Zn in Cu up to 47 per cent. Zn, then change first to the cubic, then to the rhombohedral, and finally to the hexagonal form typical of Zn. These changes correspond roughly with changes in the hardness curve. The *effect of annealing* was not appreciable.

IN the past few years much work has been done by x-ray analysis on the crystal structure of those elements which are obtainable in pure solid form at room temperature, and of many of the simpler salts and oxides.

The question arose whether this same method might not be useful and enlightening when applied to alloys.

When a compound of elements of very different atomic weights is examined by x-rays, the diffraction pattern obtained is that of the crystal structure of the heavy element alone, the intensities of the lines of this pattern being modified by the position of the atoms of the light element. This often makes the interpretation of the diffraction pattern, in terms of the complete crystal structure of the compound, extremely difficult. And the complete interpretation of the structure of a compound containing three or more elements is, in the present state of our knowledge and experience, often almost impossible, even though the x-ray diffraction pattern may be perfectly definite.

For this reason we started with very simple and well-known series of binary alloys of metals whose atomic weights differed from one another

only a little, so that we could be sure that they would both reflect x-rays in nearly equal amounts.

We used the Hull method[1] of x-ray analysis. Instead of powders we usually took fine filings, as many of our alloys were not brittle enough for powdering. The samples were prepared by mixing the filings with collodion or zapon and drying the paste to a thin sheet on glass. Such a sheet or film could be readily peeled off when dry and had the advantage of containing very little foreign material, and that little amorphous. Being composed of the light elements C, H, O, etc., quite transparent to x-rays, such a film, when placed in a narrow beam of x-rays, produces very little fogging.

The following data cover work done on nickel-iron, cobalt-iron, and copper-zinc alloys.

NICKEL-IRON ALLOYS.

Iron and nickel are known to form an unbroken series of solid solutions of all compositions from 100 per cent. iron to 100 per cent. nickel, though it has been suggested[2] that a compound may exist at 34.45 per cent. nickel (Fe_2Ni). As can be seen below, our work gave no indication of such a compound. The samples used in our work were prepared by the fusion of pure Swedish iron and pure nickel in a hydrogen resistance furnace. They therefore contained no carbon, and the percentage of other impurities was very low.

The crystallographic structure of alloys of different composition was determined, as shown in Table I.

TABLE I.

Nickel-Iron Alloys.

Per Cent. Ni.	Structure as Shown by X-ray Diffraction Patterns.
0	Centered cubic alone.
10	" " "
15	" " "
20	" " "
22	" " "
25	Centered cubic plus face-centered cubic.
27	" " " " " "
30	Face-centered cubic alone.
50	" " " "
75	" " " "
100	" " " "

There is no indication of a change in structure at 34 to 35 per cent. Ni, the composition of invar.

[1] A. W. Hull, PHYS. REV., 10, 661, 1917. J. A. C. S., 41, 1168, 1919.

[2] Chevenard, Rev. de Metallurgie, 11, 841. Weiss, Tran. Faraday Soc., 8, 149. Weiss & Foex, Arch. des Sc. Phys. et Nat. (4), 31, pp. 4 and 89.

Fig. 1 shows the equilibrium diagram determined thermally as given in the circular issued by the Bureau of Standards: "Invar and Related Nickel Steels," with a small addition below it showing the structure as determined by x-ray analysis. The agreement is fair, and might be better below 22 per cent. Ni if the x-ray method were capable of detecting very small percentages of a crystal form. That is to say, though the x-ray pictures show a pure centered cubic form at 20 per cent. Ni, there might be one or two per cent. of the face-centered cubic form present. A ten to one artificial mixture of iron and nickel (*i.e.*, centered cubic with face centered cubic structure) showed both forms quite distinctly, but we have not tested mixtures containing smaller percentages of nickel.

Fig. 2 shows the diffraction patterns as photographed from some of the alloys of this series.

These patterns prove that nickel atoms can be substituted for iron atoms in the iron (centered cubic) crystal lattice until about 20 per cent. of the iron has been so replaced. On the other hand, iron can substitute for nickel in the nickel face-centered cubic lattice to a much greater extent; *i.e.*, until about seventy per cent. of the nickel atoms have been replaced by iron atoms. These replacements are possible because the atomic volumes of iron and nickel are nearly the same, iron being 7.2, nickel 6.7, and the shapes of the atoms are nearly enough alike to make substitution possible with little strain of the intra-atomic forces. Some of the photographs show, along the edge, a scale which we occasionally used. It consisted merely of a thin sheet of molybdenum in which slots were cut at spacings calculated so as to read Ångstroms direct on the photograph.

It will be noted that the transition from the centered cubic form to the face-centered cubic form takes place between 22 and 30 per cent. Ni. This is also the region in which some of the physical properties of the ferro-nickels have maxima or minima, such as hardness,[1] tensile strength,[1] magnetic saturation intensity[2] and hysteresis losses,[3] though most of the properties investigated[4] have maxima or minima at about 35 per cent. Ni,[4] this being the reason for the assumption of the compound Fe_2Ni.

The density, electrical resistance and elasticity of ferro-nickels in this transition range (20 to 30 per cent. Ni) varies with the history of the

[1] Circular of the Bureau of Standards, No. 58 (Invar and Related Ni steels).

[2] Yensen, Journ. A. I. E. E., April, 1920, p. 396.

[3] Honda, Sci. Reports. Tohoku Inys. University, 7, p. 59, 1918.

[4] Ingersoll & Others, PHYS. REV., 16 (2), 126.

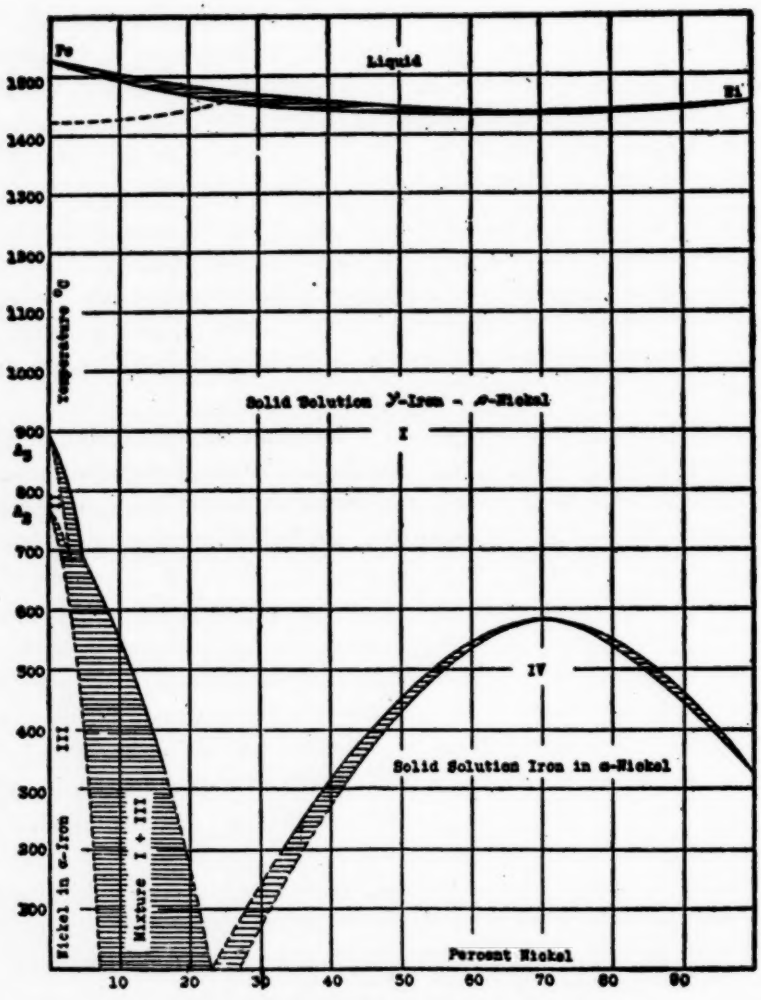

FIG. 1.—*The iron-nickel equilibrium diagram*

Structure by X-Ray Analysis		
centered cubic	Mixture	Face-centered cubic

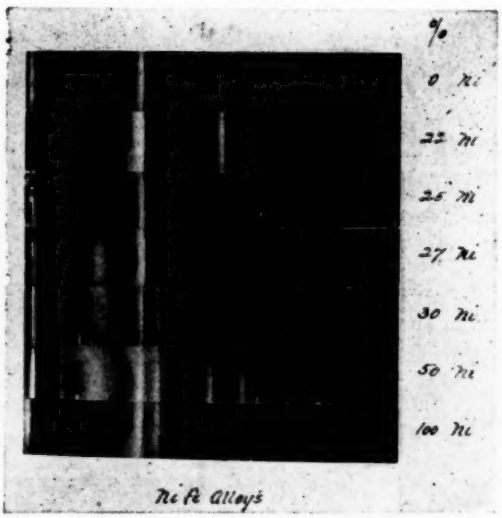

Fig. 2.

Fig. 3.

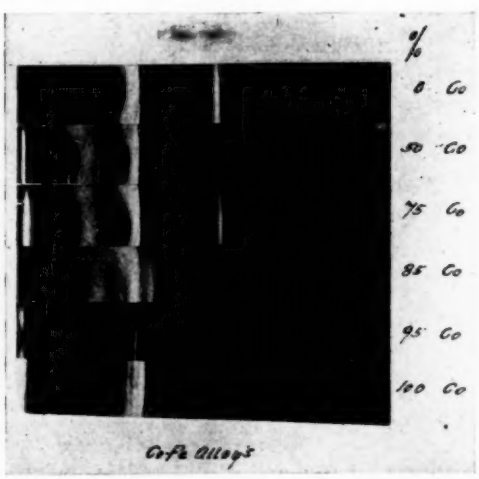

Fig. 4.

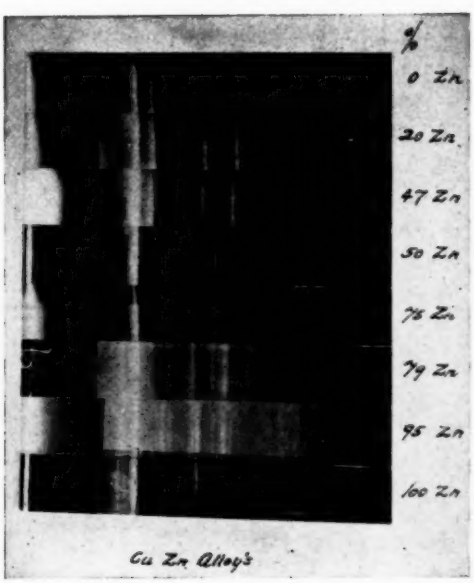

Fig. 6.

MARY R. ANDREWS.

specimen,[1] and this effect is also very marked with the magnetic properties.[2] The magnetic transformation curves as determined by Hegg[3] and others show a wide difference between the temperature of transformation on heating and on cooling for alloys between twenty and thirty per cent. nickel. If the alloys are free from carbon and manganese, both these curves lie above room temperature, and the alloys are, therefore, always magnetic at room temperatures. But if a few tenths of a per cent. of carbon be present, or a little manganese, these transformation curves are lowered so that it is possible to obtain an alloy that will be at room temperature, either magnetic or non-magnetic; *i.e.*, the irreversible alloys. If it has been cooled from a sufficiently high temperature it will be non-magnetic. If warmed from a low temperature, it will be strongly magnetic.

The alloys which were used for the photographs shown on Fig. 2 were all apparently so free from carbon, etc., that their transformation curves both lay above room temperature, as they were all strongly magnetic. But I obtained from the Bureau of Standards a sample of almost entirely non-magnetic nickel steel containing 20.1 per cent. Ni, which I photographed before and after chilling with liquid air. (See Fig. 3.) These photographs were made on the solid samples, since filings were always magnetic. The rod was filed to a wedge and the edge of this wedge was placed just in the beam of x-rays. I made photographs on samples which had been freshly filed down, and then on the same samples etched off slightly with hydrochloric acid, to determine whether there was a change at the surface due to the filing off, sufficient to show on the photographs, but could detect no difference in the pictures. However, on chilling for two or more hours in liquid air, there is, as the photographs show, a marked development of the centered-cubic form which was absent or very faint in the non-magnetic material. This test was made three times, and in every case the centered-cubic structure developed to a considerable extent. As nearly as possible the same surface of the alloy was exposed before and after chilling. The surface remained bright and free from rust or tarnish in two of the cases. In the third, the interval that elapsed between chilling and photographing was so long, due to difficulties with the x-ray apparatus, that a slight tarnish developed. This was wiped off as much as possible with a soft cloth. The penetration of the rays used is probably, for these alloys, sufficient to give

[1] Hopkinson, Proc. of the Royal Society, 48, 1; 50, 121.

[2] Honda, Idem.

[3] Archives des Sciences Physique et Naturelles, Vol. 30, p. 15.

the structure at a hundred or more microns depth, so that a very slight surface change would not affect the photograph to any extent.

This development of the cube centered form is interesting. It is an increase of the form characteristic of the stronger and more magnetic component of the alloy, iron, and therefore a decrease in the form (face-centered cubic) characteristic of the weaker and less magnetic component, nickel. Moreover, the centered cubic form is less closely packed than the face-centered, which would account for the change in density found by Hopkinson. Why the specific resistance should decrease, as he found, with an increase of the iron form, is less clear. These photographs would indicate that magnetic properties and crystal structure are closely connected, but it is not to be assumed that the centered cubic structure is necessarily magnetic. Chromium, molybdenum, and tungsten all occur in this system, and their magnetic properties are at best extremely feeble.[1]

It is to be noted that this non-magnetic alloy had a pure face-centered form, whereas the ferro-nickels of about the same composition, shown in Table I. and Fig. 2, which were magnetic, show a cube-centered form, the form that develops on chilling the non-magnetic alloy.

Small amounts of manganese, chromium, carbon, etc., doubtless influence the exact compositions at which the transition from cube-centered to face-centered form occurs. For instance, a sample of nickel steel prepared by Mr. A. W. Merrick, of the General Electric Company, which contained manganese and carbon, showed strong face-centered and weak centered cubic form, though it contained only about 18 per cent. nickel. It was weakly magnetic.

The whole question of magnetism of metals and alloys, including the Heusler alloys, offers a most fascinating field for investigation by x-rays, and I hope later to be able to do some work along these lines. A single Heusler alloy, sent to Dr. Hull by Dr. S. J. Barnett of Carnegie Institution, which was photographed, showed a centered cubic form.

Cobalt-Iron Alloys.

Cobalt and iron, like nickel and iron, form an unbroken series of solid solutions. The atomic volume of cobalt is 6.85, of iron 7.2. The equilibrium diagram as given by Guertler,[2] shows a transformation curve that breaks at about 80 per cent. cobalt. Our photographs (see Fig. 4) show the centered cubic (iron) form for alloys from 0 to 80 per cent. cobalt, then the face-centered form begins to develop, so that at 85 per cent. Co we have both forms together, and above this percentage of

[1] A. W. Hull, The Positions of Atoms in Metals, Trans. A. I. E. E., 1920.

[2] Metallographie, 1 Band, Die Binäre Legierungen, p. 78.

cobalt the face-centered form only occurs. The alloy containing 98 per cent. of cobalt showed a trace of the hexagonal form, but chiefly the face-centered cubic. Pure cobalt crystallizes in both the face-centered and the hexagonal forms.[1]

TABLE II.

Cobalt-Iron Alloys.

Per Cent. Co.	Crystal Structure by X-ray Diffraction Patterns.
0	Centered cubic.
20	" "
30	" "
50	" "
75	" "
80	" "
85	Mixture.
90	Face centered cubic.
95	" " "
98	" " " plus trace of hexagonal.
100	" " " " hexagonal.

The physical properties of the iron-cobalt alloys do not seem to be connected with this crystal structure. Yensen[2] has done a vast amount of work on the magnetic properties, and finds that the magnetic permeability increases with increase in the per cent. of cobalt, up to 34.5 per cent. cobalt (Fe_2Co), being at this point about 13 per cent. higher than pure iron, but that further addition of cobalt reduces the permeability. Honda[3] finds that the thermal and electrical conductivity decrease from 0 to 10 per cent. cobalt, increase to 65 per cent., decrease to 90 per cent., and then increase to 100 per cent. cobalt.

COPPER-ZINC ALLOYS.

The atomic volumes of copper and zinc differ rather widely, that of copper being 7.1 and of zinc 9.17. Therefore, only about half of the series forms solid solutions. Table III. shows the crystal structure of the alloys examined, and Fig. 5 the transformation curve for the copper-zinc alloys taken from Guertler,[4] below which has been sketched the divisions into crystal forms as shown by the x-rays. Type IV. of Guertler's diagram does not appear in the x-ray forms, at all. The pattern obtained from the alloys containing 79 and 82 per cent. zinc, agreed very well with the curves, to which we had access, prepared by Drs.

[1] A. W. Hull, ibid.

[2] Trans. Am. Electrochem. Soc., Vol. 32, p. 165.

[3] Sci. Reports Tohoku Imp. Univ., Vol. 8, p. 51.

[4] Metallographie, 1. Band, p. 459.

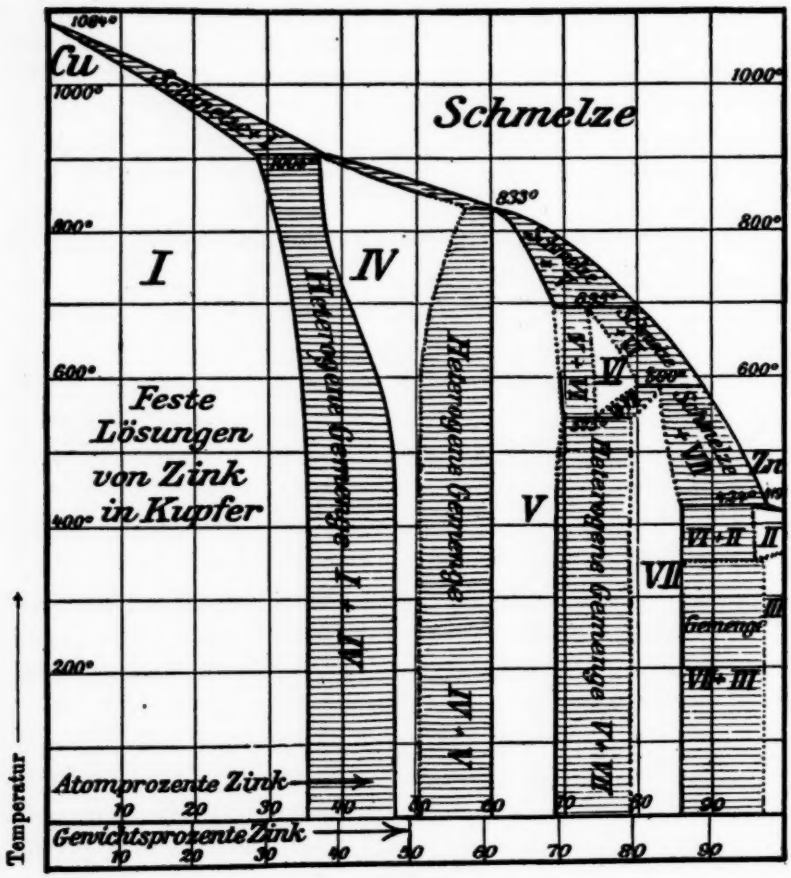

Fig. 189.
Zustandsdiagramm der Kupfer-Zink-Legierungen.

Face centered cubic
Mixture
Centered cubic
Mixture
Rhombohedral
Mixture
Hexagonal

Fig. 5.

Hull and Davey,[1] for the rhombohedral form if taken at an axial ratio of .5. Some of the photographs are shown in Fig. 6.

TABLE III.

Per Cent. Zinc.	Crystal Structure as Found by X-ray Diffraction Patterns.
00 (pure Cu)	Face-centered cubic.
20	" " "
31	" " "
37	" " "
47	Mixture face-centered cubic and centered cubic.
50	Centered cubic.
63	" "
69	Mixture.
79	Rhombohedral.
82	"
90	Mixture rhombohedral and hexagonal.
94	" " " "
100	Hexagonal.

While there is voluminous literature on the copper-zinc alloys, most of it is confined to the commercial brasses and Muntz metals; *i.e.*, the alloys containing less than fifty per cent. zinc. These are all solid solutions of zinc in copper.

The Lunkenheimer Company has, however, been kind enough to allow me to print the hardness curve shown in Fig. 7 which was deter-

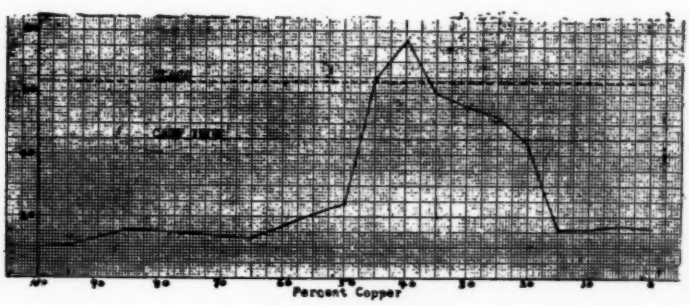

Fig. 7.

mined by Mr. G. K. Elliott, of that Company, with the Shore Scleroscope. This curve agrees roughly with the divisions of crystal forms.

We tried the effect of annealing on a number of samples, but did not find that this treatment caused any change of structure.

Calculating the density of the alloy containing fifty per cent. of each component, which showed pure centered cubic structure, gave a value of 8.17. Maey[2] gives 8.14.

[1] PHYS. REV., Feb., 1921, p. 266.

[2] Zeit. Phys. Chem., 38, 299.

We conclude that this method should be useful in determining the structure of other series of alloys.

Finally, I wish to express my hearty thanks to Dr. A. W. Hull, under whose direction this work was done, for the interest he has shown and for his many helpful suggestions.

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